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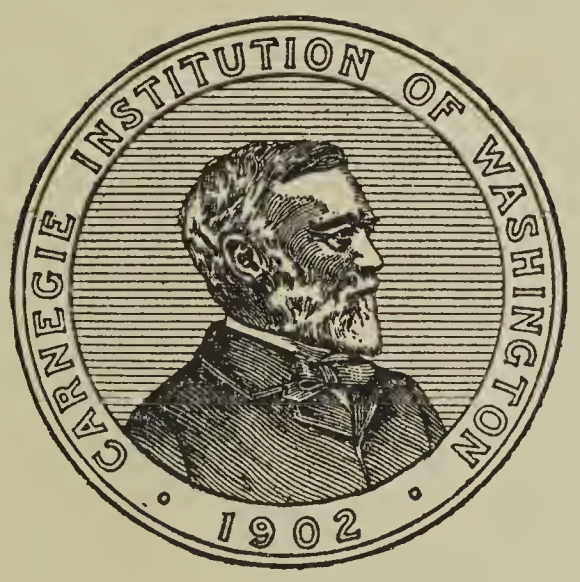

1928

W. F. ROBERTS COMPANY

STANDARD ENGRAVING COMPANY

WASHINGTON, D. C.

CATHODO-LUMINESCENCE

AND THE

LUMINESCENCE OF INCANDESCENT SOLIDS

BY

E. L. NICHOLS, H. L. HOWES, AND D. T. WILBER

PUBLISHED BY THE CARNEGIE INSTITUTION OF WASHINGTON

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CATHODO-LUMINESCENCE
AND
CANDO-LUMINESCENCE

BY

E. L. NICHOLS, H. L. HOWES, AND D. T. WILBER

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INTRODUCTION

Luminescence, in the broad sense of that term, as intended by Eilhardt Wiedemann,[1] who introduced it into our literature, covers all forms of light radiation, excepting those proper to the radiating body by virtue of its temperature. The upper temperature range of luminescence above which, like the magnetism of iron, it rapidly diminished and then vanished altogether, has, until very recently, been supposed to lie well below the red heat. Lenard[2] measured these limiting temperatures in the case of the luminescent sulphides, with results quite in accord with the findings of earlier observers and abundantly verified since.

According to the generally accepted and altogether logical view, the only departures from black-body radiation to be looked for at temperatures of incandescence must be in the nature of a deficiency, never of an excess. Selective radiation, as in the case of erbium, neodymium, etc., or of incandescent vapors, could at no point cross the envelope which corresponds to the distribution of intensities in the spectrum of the ideal black body at the temperature in question.

Of late years, however, evidence has been accumulating of the existence of agencies other than temperature which produce visible radiation within the range of incandescence. There has therefore been a great extension upward of the temperature range of luminescence. To bring together investigations bearing upon the relations between these two types, the luminescence of incandescent bodies and of the better known luminescence of substances at ordinary temperatures, is the chief purpose of the present monograph.

The Principle of Essential Identity

To facilitate the discussion the following principle, the basis for which is largely contained in the investigations herein to be described, is stated in advance of its experimental demonstration.

(1) Two spectra are essentially identical when all their components are members of the same set or sets.

(2) A *set* (as used here) is an aggregate of equidistant bands or components, where distance is measured in frequency units.

(3) A *full set* is a set in which all the members between the two outer limits of the spectrum are present.

[1] E. Wiedemann. Wied. Ann., 34, 446, 1888.
[2] Lenard and Klatt. Ann. Phys., 15, 225, 1904.

(4) An *incomplete set* is one with missing members, but in which distances between existing members are always exact multiples of the frequency interval. Sets in the spectra of solid solutions are in general incomplete—or perhaps seemingly so because of the inadequacy of our methods to pick up the weaker members of the set or those which are most completely submerged.

(5) The spectra to which this definition applies are spectra made up of bands either separate or overlapping. The structure in question has been found to occur even where the overlapping is so complete that the components are entirely submerged and the spectrum appears to be continuous. So far as known, all luminescence spectra are of the above types.

(6) The luminescence spectra of solids containing a given activator are *essentially identical.* In other words, they are made up of components belonging to the same set or sets. While the relative intensities of the components or groups of components vary with the solvent, the sets of components present in the spectrum *depend only upon the activator.*

To distinguish between the luminescence of incandescent bodies and the well-known effects which occur below the temperature of extinction as the result of photo-, cathodo-, tribo-, chemi-excitation, etc., it is proposed to refer to these latter, irrespective of the type of excitation, by the time-honored terms of *fluorescence* for the glow during excitation, and *phosphorescence* for the after-glow.

The demonstration of the foregoing principle is of necessity preceded by the experimental verification of statement (5), *i. e.*, that luminescence spectra are made up of overlapping and more or less completely submerged components. This fact was first established for certain luminescent sulphides,[1] then for the fluorescence spectra of certain calcites,[2] and finally in a much broader and comprehensive manner through the exhaustive investigations of cathodo-luminescence by Tanaka.[3] These three demonstrations will be given here from original sources in the order named above.

[1] Nichols. Proc. Am. Philos. Soc., LVI, p. 258 (1917).
[2] Nichols, Howes and Wilber. Phys. Rev.; (2) XII, p. 351 (1918).
[3] Tanaka. Journ. Opt. Soc. Am., VIII, p. 287 (1924).

PART I

CATHODO-LUMINESCENCE

(FLUORESCENCE AND THE AFTER-GLOW)

With one hundred and eight text-figures

CHAPTER I

SPECTRAL STRUCTURE OF THE PHOSPHORESCENCE OF CERTAIN SULPHIDES

Ph. Lenard, to whom we owe extended studies of the class of highly phosphorescent substances known as the Lenard and Klatt[1] sulphides, describes[2] the spectrum of the emitted light as consisting of a single broad band in the visible spectrum. This band, which appears single in most cases as viewed with the spectroscope, does not, however, conform to the recognized criteria. The marked difference between the color of fluorescence and that of phosphorescence and the changes of color during decay, suggest overlapping bands. E. Becquerel[3] in 1861 showed, in his pioneer work on phosphorescence, that the color of the emitted light varies with the wave-length of the exciting light. His observations apply, it is true, to sulphides of barium, calcium, and strontium, not identical in make-up with the sulphides of Lenard and Klatt, but obviously belonging to the same class. Some years ago[4] one of the present writers gave more direct evidence of the existence of more than one band in the spectra of these substances. In that investigation, which dealt primarily with the phenomena of color as seen in the phosphorescence, it was shown that with the aid of a special form of phosphoroscope[5] which permitted the observation of phosphorescence during the first few thousandths of a second after the cessation of excitation as well as later, various marked changes of color during decay not previously noted could be detected. These changes were readily explained by the assumption of overlapping bands, one of which decays with great rapidity and vanishes in a few thousandths of a second, while the other persists. The actual existence of these two components was readily verified: (1) by observing the spectrum of the light as viewed through the openings of the phosphoroscope; (2) by exciting the substance at the temperature of liquid air.

EFFECTS DURING DECAY

Variations in the brightness of phosphorescence with the time find convenient indication by means of the curve of decay; and the effects

[1] Lenard and Klatt. Ann. der Physik., XV, p. 225, 1904.
[2] Lenard. Ann. der Physik, XXXI, p. 641, 1910.
[3] E. Becquerel. La Lumiere Vol. I, 1861.
[4] Nichols. Proc. Am. Philos. Soc., 55, p. 494, 1916.
[5] Nichols. Proc. Nat. Acad. Sc., II, p. 328, 1916; also Nichols and Howes. Science, n.s., XLIII, p. 937, 1916.

of temperature, etc., on the intensity are capable of graphical or analytical expression. The subtle and fleeting changes of color which occur as the phosphorescence dies away or when the substance is heated or cooled or when we compare sulphides varying in composition, do not lend themselves so readily to such methods of expression. The effects must be seen to be appreciated, whence it seemed of interest to try to record some of the phenomena by means of color photographs.

Now, the glow of even the brightest of these phosphorescent substances is in reality of very low intensity, and color-plates such as the Lumiere plates used in the experiments to be described are relatively slow. The total light effect obtained by a single excitation is inadequate for the proper exposure of the plate when used in the camera in the ordinary manner. Indeed, it was found in some preliminary trials by Professor G. S. Moler that even a plate placed in immediate contact with a tube containing the phosphorescent sulphide as soon as practicable after intense excitation and allowed to remain for several minutes or until the whole of the total light effect had been utilized, was decidedly underexposed. On the other hand, the color effects to be recorded change rapidly, especially during the first few hundredths of a second after excitation, so that it was necessary to obtain the equivalent of a large number of successive short exposures, each made at the particular time after excitation for which the color record was desired.

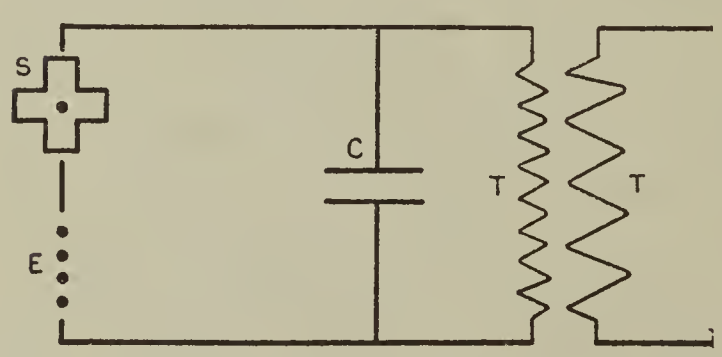


FIG. 1—Electrical circuit of the synchrono-phosphoroscope

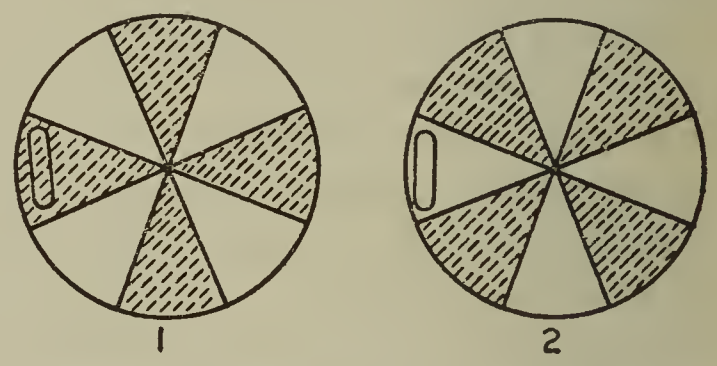


FIG. 2—Revolving disk of synchrono-phosphoroscope

To this end a special form of phosphoroscope was constructed, by means of which the substance, inclosed in a flat tube of glass about 10 cm. long and from 1 to 1.5 cm. wide, was viewed through a revolving disk with alternate open and closed sectors of 45° aperture. The disk was mounted on the shaft of an alternating-current synchronous motor on a 60-cycle circuit and excitation was by a series of fine sparks (*E*, fig. 1) between zinc terminals. The sparks were produced by the action of the secondary coil of a small step-up transformer with a condenser (*C*) in the same circuit. A spur-wheel of zinc (*S*) was mounted on the shaft of the motor and its four arms

passed the two terminals of the sparking circuit with an air-space of about 1 mm. The wheel was adjusted so that this passage coincided with successive crests of the alternating-current wave and the sectored disk was shifted until the sparking occurred during eclipse, *i. e.*, at the time when a closed sector obscured from view both the sparks and the substance under excitation (see fig. 2, position 1).

With this arrangement the specimen, which was mounted vertically in a line parallel to the row of spark-gaps and distant from them about 2 cm., was intensely illuminated 120 times a second and was visible during intermediate intervals of 1/240 second, each beginning about 0.0001 second after excitation ceased (see fig. 2, position 2). For observations during later stages of decay, the wheel could be driven slowly by means of a direct-current motor or moved stepwise an eighth of a revolution at a time at the desired rate.

Since some of the most striking changes of color are produced by differences of temperature, the tube containing the phosphorescent sulphide was mounted within a cylindrical Dewar flask with unsilvered walls. The lower end rested in a metal mercury cup, while the upper end passed through a heating coil (see fig. 3). From the bottom of the mercury cup, *M*, a copper rod projected downward into liquid air. The region at *A* could thus be maintained at a temperature of +20° C., or higher, while the lower end at *B* was at approximately —185° C. A fairly stable temperature gradient soon established itself and the colors of phosphorescence through the entire range could be observed and photographically recorded.

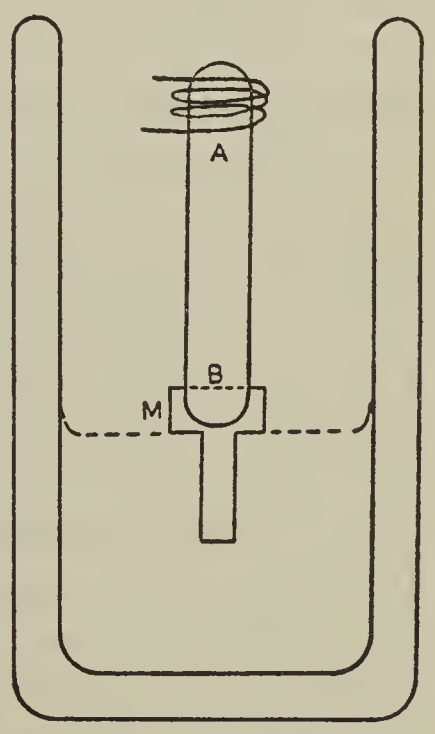


FIG. 3—Liquid-air bath for phosphorescent sulphides

Excitation under these conditions was obtained by inserting the sparking device within the Dewar flask and many photographs were made in that way; but this is a procedure demanding special precautions, as the atmosphere above the liquid air is very rich in oxygen and conflagration of the insulating materials and even of the metal part is likely to occur.

The principal phenomena to be studied were those due to (1) the change of color during the decadence of phosphorescence; (2) the effect on the color of phosphorescence when the temperature of excitation varies between +20° C. and —185°.

CHANGES DURING DECAY

To observe the color-changes during decay it is only necessary to mount the sulphide in the phosphoroscope and excite with the disk

running at normal speed, *i. e.*, 1,800 revolutions a minute. If the excitation be stopped by breaking the spark-circuit, the changes of color as phosphorescence dies away can be followed for several seconds.

In the case, for example, of a sulphide known as No. 33 (Ba, Cu, $Na_2B_4O_7$), the initial tint of red-yellow changes to a deep red. Another of the preparations of Lenard and Klatt, No. 3 (Ca, Bi, Na_2SO_4; CaF_2, $Na_2B_4O_7$), which is typical of many, appears bluish green through the revolving disk and changes very quickly after the close of excitation to a deep violet.

The work of Lenard and others, using a very different procedure, has shown the spectra of these substances to consist of broad overlapping bands distinguishable from each other chiefly by the mode of excitation, duration, and the influence of temperature; and it is clear that in these and similar cases we have to do with two or more such bands.

In the first of these two examples the change of color may obviously be explained by the more rapid decay of the band of shorter wave-length; an hypothesis readily verified by observing the substance as seen through the disk with a spectroscope. What appears as a single very broad band collapses promptly from the green end when the exciting circuit is broken, leaving the red portion only, which persists for many seconds.

We have to do, then, with a combination of a band of very short duration (having its crest in the green) and a band of long duration in the red; and the color at any time after the close of excitation is the sum of the instantaneous values of the two components. Since the decay of the green band is very rapid indeed, its intensity becoming negligible in a small fraction of a second, the appearance of the phosphorescent surface when observed by ordinary methods is chiefly due to the red component and it appears of a much more ruddy color than when viewed through the rapidly revolving disk. The same is true of all the other barium sulphides studied.

The Ca and Sr sulphides in general appear as greenish blue, pure blue, or even violet as in the example cited (No. 3) when viewed in the ordinary manner; but in the phosphoroscope they are green, going over into the blue or violet after the cessation of the periodic excitation. Here, obviously, we again have to do with two bands of which the green is of very short duration, while it is not in this case the band of longer wave-length which persists, but that of greater refrangibility. It appears in general that these sulphides fall into two distinct classes: Those of which the persistent band is of longer wave-length, *i. e.*, red, chiefly if not exclusively barium sulphides, and those of which the persistent band is of shorter wave-length.

Thirty-four sulphides examined by the method just described showed color changes in accordance with the foregoing classification.

COLOR CHANGES DUE TO COOLING

Since the intensity of the band of rapid decay vanishes in a small fraction of a second, ordinary observations of the phosphorescence of these sulphides pertain, as has already been pointed out, to the persistent band alone. It is not possible to isolate the rapid band by the use of the phosphoroscope, since during the brief period immediately following excitation both bands are present and the color is that due to their combination. The slow bands, however, are greatly diminished by cooling the phosphorescent substance and are often reduced almost or quite to the vanishing-point. Thus it is possible, by lowering the substance to temperatures approaching that of liquid air, to observe the color and intensity of the rapid band by itself. When, for example, we cool the lower end of a tube of the BaCu sulphide (No. 33), as described in a previous paragraph, and watch its phosphorescence through the sectored disk, the red-yellow of the upper (warm) end merges gradually into a brilliant green

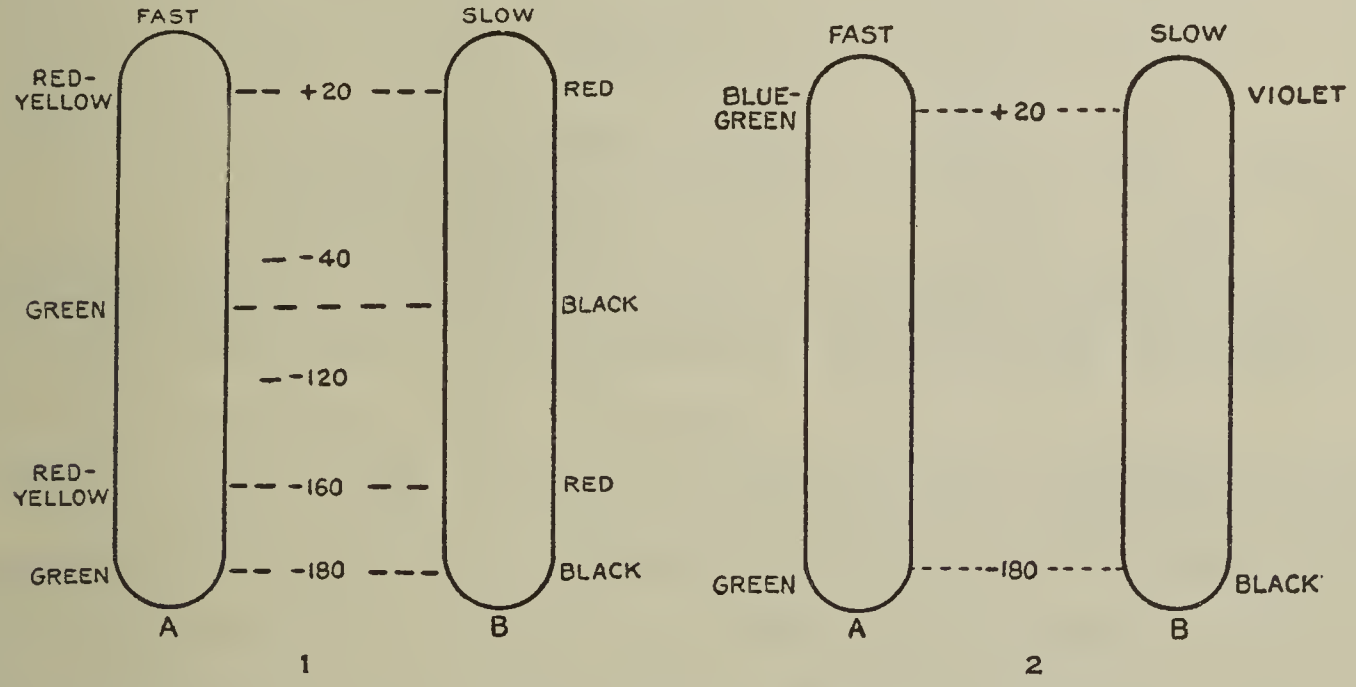


FIG. 4—Color changes due to cooling. Fast and slow from —180° to +20°. (1) Red end; (2) violet end

occupying the cooler regions below. A red-yellow patch occurs still lower down, while at the very bottom, where the temperature approaches that of liquid air, there is a return to green. The distribution of colors and approximate temperatures are indicated in figure 4 (1) *A*.

That this remarkable distribution of colors is to be interpreted as the result of the killing off of the "slow" red band by cooling and its subsequent recurrence at about —160° is beautifully confirmed by the appearance of the tube after the entire cessation of excitation. When the spark-circuit is broken, the green vanishes at once, but the

red regions above and below continue to glow for many seconds, as indicated in figure 4 (1) *B*.

In 1910 one of the writers measured the change in the phosphorescence of this substance[1] effected by temperature. The curve, which is reproduced in figure 5, applies to the red band only, since the green band would have vanished long before observations of brightness could be made by the method then employed. It describes exactly the appearance noted in figure 4 (1) *B*, *i. e.*, a rapid diminution on cooling, complete disappearance at about —120° C., a recurrence of measurable intensity below —140°, with a maximum at —160°.

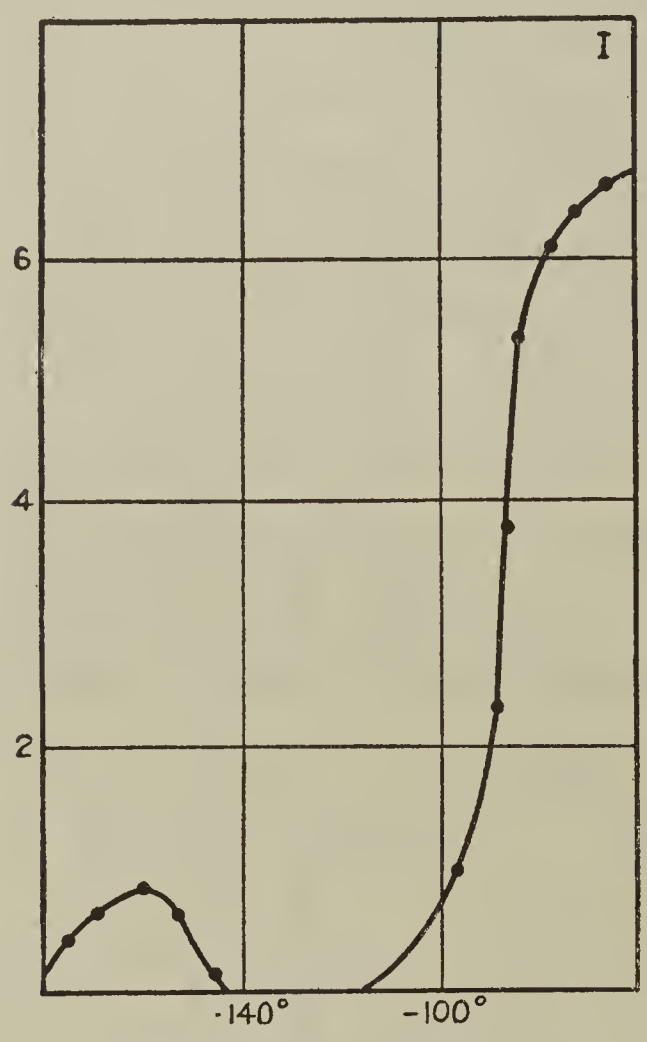


FIG. 5—Effect of low temperatures on brightness of phosphorescence

All BaCu combinations, so far as examined, have a red-yellow color of phosphorescence at room temperature, with the red band of longer duration; but the relative intensity of the red varies greatly with different fluxes and proportions. While the persistence of the green band at low temperatures seems to be a general property of these substances, the recrudescence of the red, as in the example here considered, is not always apparent. In other substances of this class it is either masked by the brightness of the green component or entirely absent.

The effect of cooling the phosphorescent sulphides of calcium and strontium is analogous to that just described. The band of long duration is greatly weakened or disappears; the other, which in all the cases so far studied is a green band, persists. Since the band destroyed by cold is, however, blue or violet, the change of color is the reverse of that noted in the barium compounds, *i. e.*, from blue or blue-green to green instead of from red-yellow to green. A striking example is the combination (Ca, Bi, Na_2SO_4, CaF_2, $Na_2B_4O_7$). The green-blue of early phosphorescence, as observed through the sectored disk at +20°, goes over to a full green in the cold portions of the tube, the phosphorescence of long duration being a rich pure violet. (See fig. 4 (2).)

[1] Nichols. Proc. Am. Philos. Soc., XLIX, 275, 1910.

It should be noted in this connection that in their original paper[1] Lenard and Klatt depicted these spectra as complex, while in a later paper, already cited, Lenard prefers to regard them as single. This later view may be most briefly and conveniently indicated by the upper part of figure 6, which is a typical diagram reproduced from Lenard's plate. Here the area *Fl* represents the location of the band of fluorescence, indicated as a single broad band, and the two inclosed areas, *BB*, in the ultra-violet show the regions capable of exciting

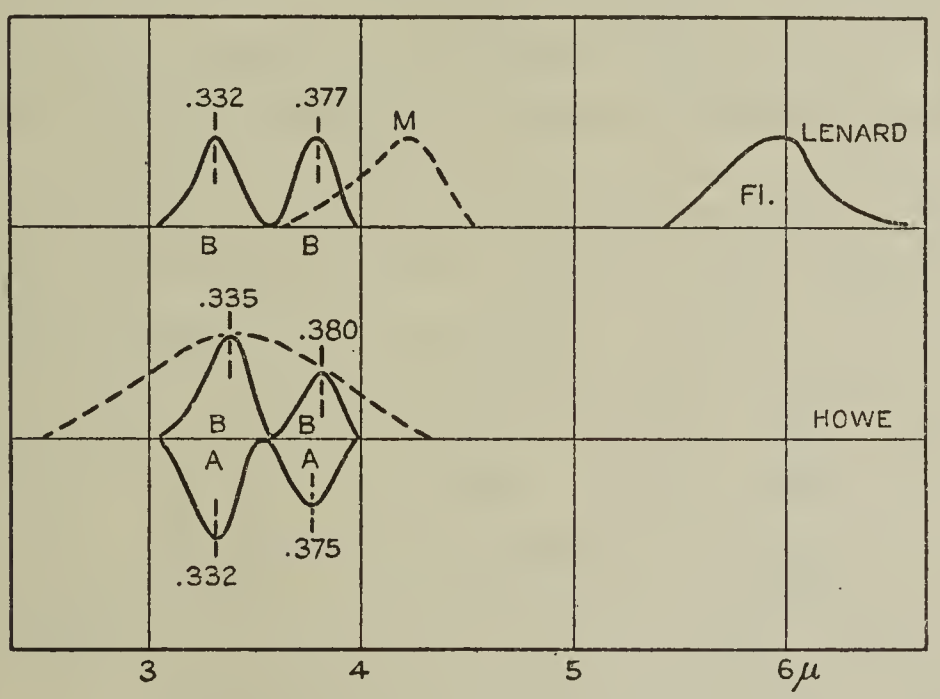


FIG. 6—Regions of selective excitation and fluorescence (Lenard). Regions of selective excitation and absorption (Howe)

phosphorescence. These two crests or so-called bands of excitation (Erregungsbände) have fixed positions as to wave-length, for each sulphide.

SIGNIFICANCE OF THE BANDS OF EXCITATION

It seemed probable that these regions of maximum excitation, the positions and appearance of which had long since been beautifully depicted by Becquerel in the work already cited, were due to the presence of absorption bands. Dr. H. E. Howe, who was engaged in the study of the ultra-violet absorption spectra of certain fluorescent solutions, was kind enough to test this hypothesis. Following the method developed by Stokes and by Becquerel and subsequently used by Lenard and Klatt, the phosphorescent substance was exposed to the dispersed rays of a large quartz spectograph. The source of light was the powerful submerged aluminum spark described by Henri[2] and subsequently employed by Howe[3] and others in the study of absorption spectra. A considerable portion of the ultra-violet spectrum was found capable of exciting fluorescence. In the case

[1] Lenard and Klatt. Ann. der Physik (4), XV, p. 225, 1904.
[2] V. Henri. Physikalische Zeitschrift, 14, p. 516, 1913.
[3] H. E. Howe. Physical Review, 2, VIII, p. 674, 1916.

of a barium sulphide with lead with a flux of sodium sulphate this broad band of excitation, corresponding to Lenard's "Momentanband," extended from 0.42μ to about 0.23μ. It is indicated by the dotted line in the lower diagram in figure 6. Upon this were gradually developed two narrow crests or maxima which glowed for some time after the close of excitation, the "Dauerbände" of Lenard. The wavelengths of these crests were estimated as 0.380μ and 0.335μ. Lenard gives for a sulphide of similar composition 0.377μ and 0.332μ respectively, as shown in the upper diagram.

To obtain the absorption spectrum of these sulphides by transmission is impracticable on account of their great opacity, but the following procedure was in some instances successful. A thin layer of the substance was pressed between quartz plates and mounted in front of the slit in such a position that rays from the spark would be diffusely reflected into the collimator of the spectrograph. Photographs which exhibited the selective absorption of the substance were thus obtained. The barium sulphide under investigation showed two narrow absorption bands, indicated below the base-line in figure 6, and a region of general absorption beyond 0.3μ. The two narrow bands whose crests as determined from the photographs were at 0.375μ and 0.332μ obviously correspond with the bands of excitation and sufficiently explain the existence of the latter.

Similar coincidences between selective absorption and selective excitation were established in the case of the compound SrPbNaF at 0.355μ (Lenard's band 0.358μ) and of SrZnF at 0.360μ and 0.297μ (Lenard's bands 0.360 and 0.297μ). The relation is therefore probably a general one, corresponding to that already demonstrated in the case of the selective action of infra-red rays upon phosphorescence of zinc sulphide, where the maximum effect was found in regions of maximum absorption.[1]

SPECTROPHOTOMETRIC MEASUREMENTS

The area marked *Fl* in the diagram, taken from Lenard's paper (fig. 6), is only intended to indicate the approximate range of fluorescence in the spectrum. It shows only what appears to the eye. The color changes during the phosphorescent after-glow described in the foregoing paragraphs imply, however, a more intricate structure, and it was in the hope of revealing more than could be discovered by ordinary spectroscopic inspection that the following spectrophotometric study of three characteristic sulphides was made by one of the present writers (Howes).

His method, briefly stated, was as follows: The substance was

[1] Nichols and Merritt. Carnegie Inst. Wash. Pub. No. 152, p. 84.

mounted behind the disk of the synchrono-phosphoroscope and was illuminated by means of the radiation of the zinc spark, the disk being adjusted so as to afford observation of the phosphorescence in its earliest stages, *i. e.*, after a few ten thousandths of a second from the close of excitation. In place of the photometer used in taking curves of decay, a spectrophotometer with two collimators, Lummer-Brodhun cube (*L*) and constant deviation prism, was mounted as shown in figure 7. One collimator was directed toward the phosphorescent surface *P*, the other toward the comparison light *A*. The latter consisted of an acetylene flame properly screened. The two slits (*S*, *S*) of the

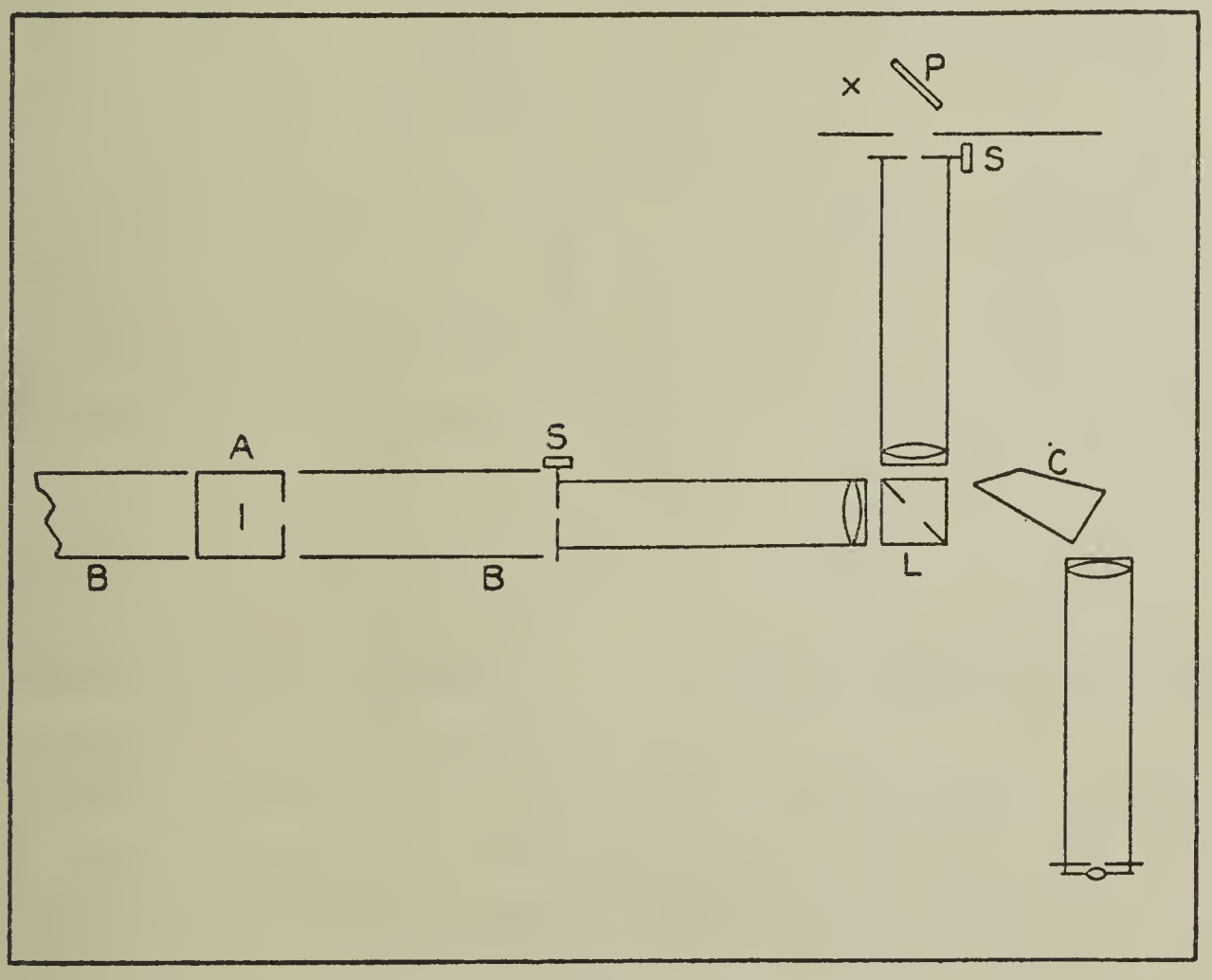


FIG. 7—The spectrophotometer

spectrophotometer were of equal width and measurements were made by moving the flame along the photometer bar (*B*, *B*) in the prolonged axis of the collimator. Settings were made at intervals of 50 Ångström units throughout the spectrum. On account of the very great range of intensities within the phosphorescence spectrum, it was necessary to increase the effective range of the photometer bar by the interposition of screens for which the reduction factors had been carefully determined.

The first substance studied in this manner was a strontium sulphide, with bismuth as the active metal, designated as L. and K. No. 13. The spectrum curve obtained using the method described above is shown in figure 8. The complexity of the band is very obvious, there being subordinate crests on either side of the principal maximum.

The curve suggests at once a group of overlapping bands, so nearly merged that to the eye it would appear as a single simple band. There is, moreover, a distinct suggestion of a systematic relation.

Taking the relative frequencies, *i. e.*, reciprocals of the approximate wave-lengths ($1/\mu \times 10^3$) of the crests as estimated from the curve, it is found that the intervals are either very nearly 58, or twice that

FIG. 8—Spectrophotometric curve of a sulphide with bismuth as activator

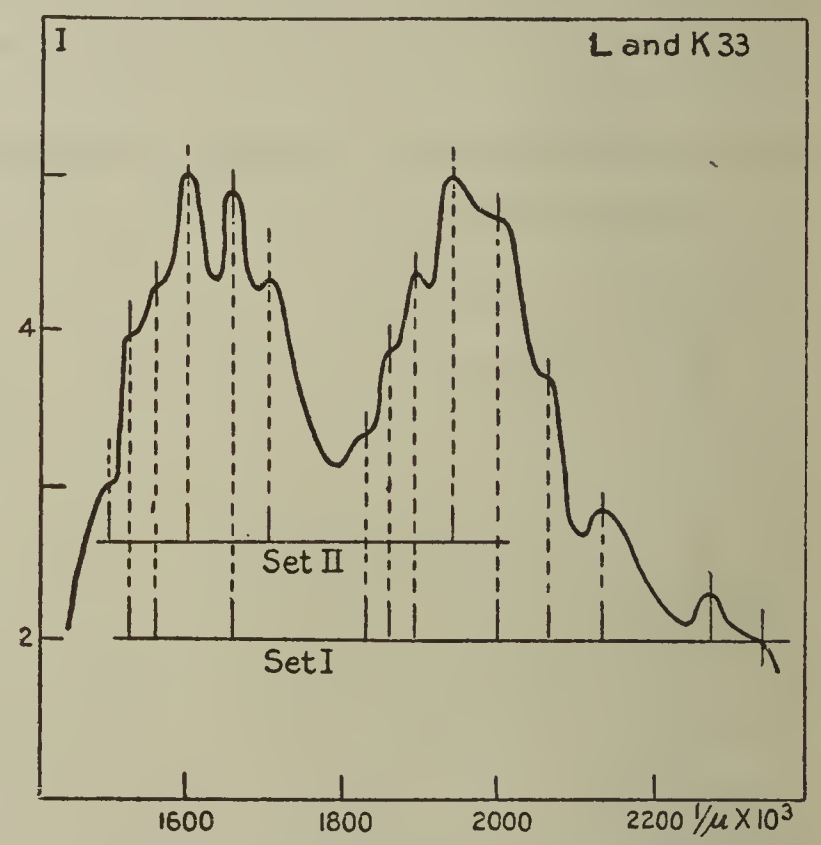


FIG. 9—Spectrophotometric curve of a sulphide with copper as activator

number. If a set having 58 as its constant interval be formed with one member located at the principal crest ($\lambda = 0.4800\mu$), other members of this set will coincide with the subordinate crests of the curve. The short vertical lines in figure 9 indicate the positions of those members of such a set as coincide with the crests, and of two further members which fall on slight and not very well defined maxima at 0.5562μ and 0.5921μ.

TABLE I.—*Components in the spectrum of the phosphorescent sulphide L and K No. 13*[1]

μ	$1/\mu \times 10^3$	Δ	μ	$1/\mu \times 10^3$	Δ
0.4430	2,257		0.4938	2,025	
		4 × 14.5			8 × 14.5
.4547	2,199		.5238	1,909	
		4 × 14.5			8 × 14.5
.4670	2,141		.5562	1,793	
		4 × 14.5			8 × 14.5
.4800	2,083		.5921	1,677	
		4 × 14.5			

[1] The activator in this strontium sulphide is bismuth.

The agreement is sufficiently good throughout to warrant the statement that *the band consists of a complex, the overlapping compo-*

nents of which, so far as visible, are members of a set having a constant interval. Table I gives the approximate frequencies and wavelengths.

At the time of this determination, which was the first serious attempt to look for submerged components in the broad bands of fluorescence spectra,[1] the frequency interval of the set of components in table I was taken as 58, but in the subsequent work of Tanaka, which was based upon these preliminary experiments and was extended to 42 different elements used as activators, the frequency-interval for bismuth was found to be of the order of 14.6. Within the experimental errors of the measurements now under consideration, we may regard this a fourth of 58, and hence we may take 14.5 as the proper interval for the set in table I.

Another phosphorescent substance with bismuth as the activator was described by Lenard and Klatt. It is a calcium sulphide and is known as L. and K. No. 3. This, when measured with the spectrophotometer, yielded a curve upon the red flank of which eight crests denoting submerged components could be located. Two of these crests belong to the set found in the foregoing study of L. and K. No. 13; the others, to sets of the same frequency-interval but displaced respectively four frequency units toward the red and eight units towards the violet (table II).

TABLE II.—*Components in the spectrum of the phosphorescent sulphide L. and K. No. 3*

Set. I[1]			Set II			Set III		
μ	$1/\mu \times 10^3$	Δ	μ	$1/\mu \times 10^3$	Δ	μ	$1/\mu \times 10^3$	Δ
0.5528	1,809		0.5300	1,887		0.5411	1,848	
		8×14.6			8×14.6			8×14.6
.5910	1,692		.5650	1,770		.5781	1,731	
					8×14.6			8×14.6
			.6049	1,653		.6200	1,614	

[1] The interval of these sets is a more precise multiple of Tanaka's value for Bi, *i. e.*, 14.6, than that given in table I, since $117 = 8 \times 14.625$. This set is identical, within experimental errors, with the set in table I.

The third phosphorescent substance tested in the course of this investigation (L. and K. No. 33) was a barium sulphide with copper as its activator. The spectrophotometric curve (fig. 9) shows at least two overlapping complexes and at least 15 partially submerged components are to be distinguished. These components can be

[1] It should be noted, perhaps, that in 1910 one of the present writers showed the banded spectrum of some samples of fluorescence to be complex (see Proc. Am. Phil. Soc., XLIX, 267-280, 1910).

arranged in two sets, with a frequency interval of 34, as shown in table III.

TABLE III.—*Components in the spectrum of the phosphorescent sulphide L and K No. 33*

Set I			Set I—cont.			Set II		
μ	$1/\mu \times 10^3$	Δ	μ	$1/\mu \times 10^3$	Δ	μ	$1/\mu \times 10^3$	Δ
0.4273	2,340		0.5365	1,864		0.5154	1,940	
		2×34			34			7×34
.4401	2,272		.5464	1,830		.5875	1,702	
		4×34			5×34			3×34
.4682	2,136		.6024	1,660		.6250	1,600	
		2×34			3×34			3×34
.4854	2,068		.6418	1,558		.6675	1,498	
		2×34			34			
.5000	2,000		.6562	1,524				
		3×34						
.5268	1,898							
		34						

The interval for this sulphide (No. 33) is the same as that later found by Tanaka for substances in which copper is the activator and set II of table III is nearly identical with series II of his table for that element.[1]

SUMMARY OF THE FOREGOING STUDY OF PHOSPHORESCENT SULPHIDES

By means of the preliminary spectro-photometric measurements just described, the following facts were established:

(1) The seemingly broad banded spectra of the phosphorescent after-glow of certain sulphides following excitation by the zinc spark are made up of overlapping and partly submerged components.

(2) These components, as revealed by irregularities in the spectro-photometric curves, may be arranged in sets in which the distance between members, expressed in frequency units, is an exact multiple of a constant called the *frequency-interval.*

(3) The frequency-interval for the two sulphides having *bismuth* as an activator, one of which was a strontium sulphide (L. and K. No. 13) the other a calcium sulphide (L. and K. No. 3) was found to be the same (14.5), from which it was inferred that the frequency-interval was independent of the solvent.

(4) Since the fluxes employed in the preparation of these two sulphides also differed, being Na_2SO_4 in the case of No. 13 and a

[1] T. Tanaka. Jour. Opt. Soc. Am., VIII, p. 304 (1924).

mixture of CaF_2, Na_2SO_4, and $Na_2B_4O_7$ in that of No. 3, it was further inferred that the frequency interval was independent of the flux.

(5) The frequency interval for the third sulphide studied, a barium sulphide with copper as activator and $Na_2B_4O_7$ as flux, was found to be 34, from which it was inferred that the frequency interval depends on the activator. The above conclusions are amply confirmed by later observations to be described in the present treatise.

CHAPTER II

THE FLUORESCENCE OF KUNZITES AND CALCITES

I. KUNZITES

That the variety of spodumene known as kunzite is phosphorescent has been known almost from the day of its discovery. In August 1903, George F. Kunz[1] described its occurrence and properties, and in September of that year Baskerville,[2] who was making an exploration of the optical properties of the minerals in the American Museum of Natural History, proposed the name of kunzite for this substance. In the course of his description he stated that although it showed no sign of fluorescence or phosphorescence when exposed to ultra-violet light, X-rays excited it to a prolonged whitish phosphorescence.

Kunz and Baskerville[3] subsequently tested the luminescence of numerous minerals and reported that kunzite was wonderfully phosphorescent under the action of radium; that ultra-violet light, contrary to Baskerville's first observation, excited certain specimens to prolonged luminescence, and that X-rays affected all the crystals of that mineral which were examined.

A writer in *Nature,* presumably Mr. F. Soddy,[4] speaks of the excitation of kunzite by radium as due chiefly to the β-rays and mentions also the powerful excitation obtained by cathodo-bombardment.

Pochettino,[5] in his extended investigation of the luminescence of minerals, included the spodumenes, and in particular certain samples of kunzite. He found this substance feebly fluorescent under the action of light with the emitted rays polarized. Under the cathode rays he was able to observe a spectrum consisting of a very strong broad band extending from λ0.690 to λ0.515 and a weak one from 0.48 to 0.42. The band of longer wave-length was of protracted phosphorescence, while that in the blue disappeared "instantly" upon cessation of the excitation. Pochettino noted further the phenomenon of thermo-luminescence at 235° C., in which case the rays were not polarized. The power of emission ceased at about 400° C.

FLUORESCENCE SPECTRA

The crystals studied by the present writers were of two kinds, (1) those with the pink or rose-lilac hue generally considered charac-

[1] Kunz, Science, 18, p. 280 (1903).
[2] Baskerville, Science, 18, p. 303 (1903).
[3] Kunz and Baskerville, Science, 18, p. 769 (1903).
[4] "F. S.," in Nature, 69, p. 523 (1904).
[5] Pochettino, Il Nouvo Cimento (V), 18, p. 245 (1909) and (VI), 1, p. 21 (1911).

teristic of kunzite, and (2) crystals nearly colorless, but with a suspicion of a green or aquamarine tint. Under the action of cathode rays both were strongly fluorescent, but the colors of luminescence differed. The pink crystals glowed with the powerful yellow-red light described by previous observers, which resembles nothing more closely than the light of some nearly transparent body, such as quartz or glass at a temperature of about 900° C. The colorless specimens emitted light of a rose-violet hue. Observed with a hand spectroscope, this difference is seen to be due to the relative strength of the fluorescence bands. In the spectrum of the light from the colorless crystals the blue band is much stronger and its intensity is such as notably to modify the color of the fluorescence.

The specimen *K* to be studied was placed in a V-shaped vacuum-tube as shown in figure 10, and the face, bombarded from above by

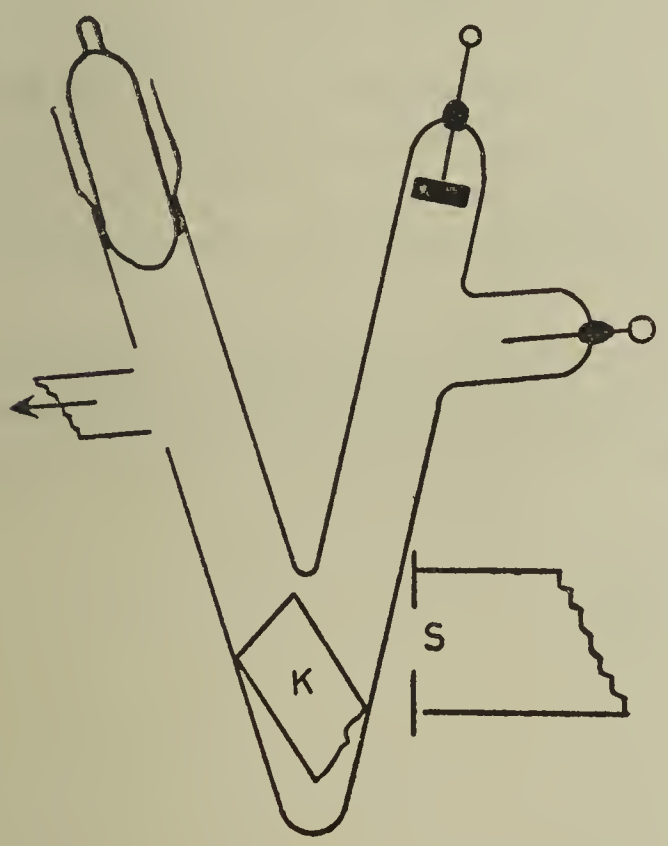


FIG. 10—Vacuum-tube for cathodo-bombardment of crystals

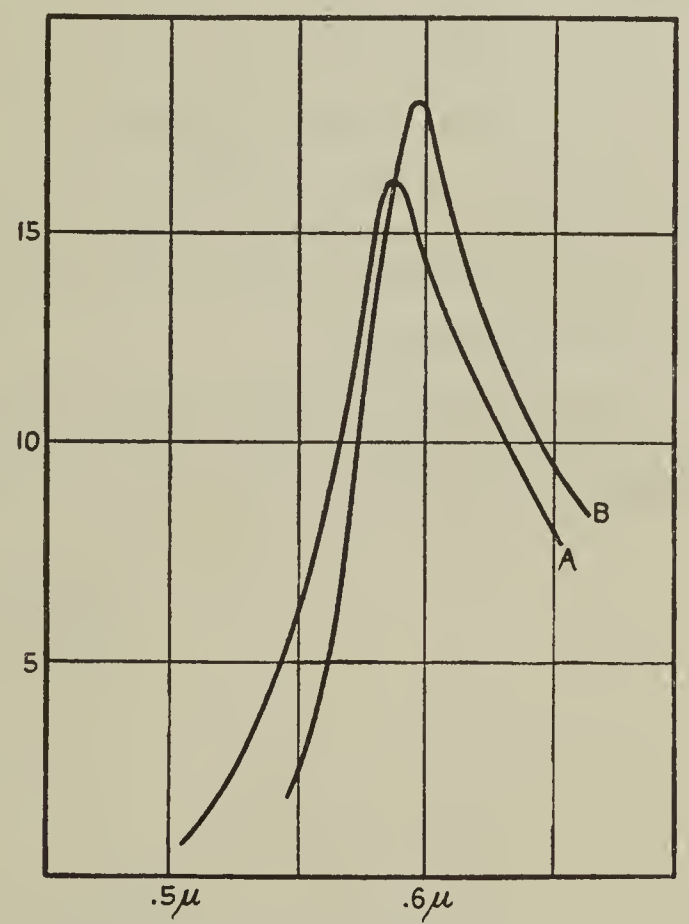


FIG. 11—Shift of fluorescence toward the red on cooling. (*A* at 20° C.; *B* at −180° C.)

cathode rays, was observed with a spectro photometer the slit of which is shown at *S*. The strong band between 0.7μ and 0.5μ was readily measured spectrophotometrically and was found to have the typical form observed in numerous other fluorescent substances and depicted in earlier work.[1]

The curve of intensities (*A*, fig. 11) is, as usual, nearly symmetrical, but somewhat steeper toward the violet. The well-defined crest is at 0.590μ. The band is really a composite of overlapping components,

[1] Nichols and Merritt, Physical Review (1), XVIII, 403, 1904; XIX, 18, 1904; XXI, 247, 1905.

as will be shown later, and the curve *A* represents, roughly, the envelope inclosing the group.

The effect of cooling, which is known to modify the character of most fluorescence spectra, was determined by immersing the tube in liquid air to a level above that of the crystal. The appearance of the fluorescence when the specimen was thus cooled was distinctly redder to the eye, and this impression was confirmed by the spectrophotometric measurements. The curve (*B,* fig. 11) which is a graphic representation of these, has its crest shifted towards the red to 0.598μ. There is a corresponding accession of the longer wavelengths and a diminution on the side towards the violet. There is no indication of even a partial resolution into a group of narrow bands such as occurs in the case of the fluorescence spectra of the uranyl salts.[1]

That a crystal thus situated in vacuo in a glass tube and subjected to the heating effect of even a very moderate cathodic bombardment will be in thermal equilibrium at some temperature considerably above that of the liquid air surrounding the tube is obvious. That this difference of temperature might be more than 100° C. was indicated by previous experience with substances subjected to somewhat similar conditions.

A modification of the apparatus enabled us to determine that even at a temperature closely approaching that of liquid air no further marked modification in the position or appearance of the band

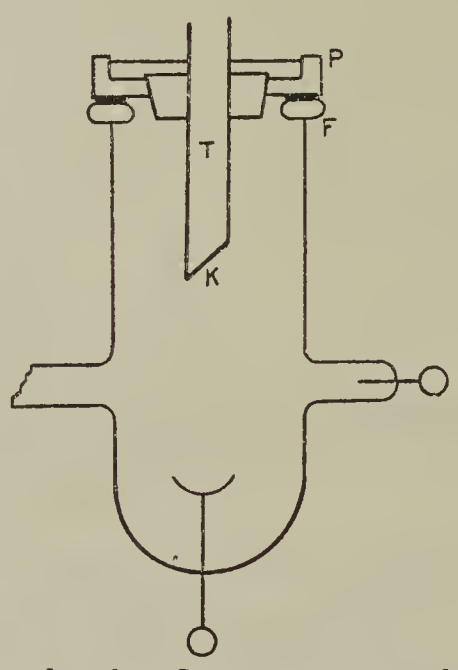


FIG. 12—Vacuum-tube for fluorescence at low temperatures

occurred. For this purpose a small piece of kunzite was powdered and cemented to the outer surface of a test-tube the bottom of which had been softened by heat and obliquely flattened so as to form a convenient target for cathode rays. This test-tube was mounted within a vacuum-tube of the form shown in figure 12, in which *P* is a cast-iron

[1] Nichols and Howes. Carnegie Inst. Wash. Pub. No. 298, Chap. V (1919).

plate ground to the flange F of an open-mouthed glass vessel having a cathode at the bottom. The test-tube T was inserted through a rubber stopper fitted to a central opening in the iron plate. When a proper vacuum had been attained, liquid air was poured into the test-tube, cooling the coating of powdered kunzite K. The fluorescence of K could be observed in the manner previously described, and any change in the character of the spectrum noted. The measurements, while less satisfactory than those indicated in figure 11, were in essential agreement with them.

The fluorescence band of shorter wave-length which begins at 0.49μ and extends into the violet, is less favorably situated for study with the spectrophotometer, and we contented ourselves with an estimation of its extent and general character by a photographic method. Spectrograms were taken, using both the pink and white crystals, upon two different plates, so as to lessen errors due to the selective sensitiveness of the photographic film. The negatives indicated that the same bands were present in both cases, but, as had already been noted by visual observations, were of very different relative brightness. The blue band was found to lie between 0.49μ and 0.40μ, with a crest at approximately 0.432μ. Since the location of the crest by visual inspection was rather uncertain, one of the negatives was measured as to density step by step at intervals of 1 mm. by means of a photo-electric cell. This determination, which was kindly made for us by the late Dr. W. G. Mallory, gave boundaries and location

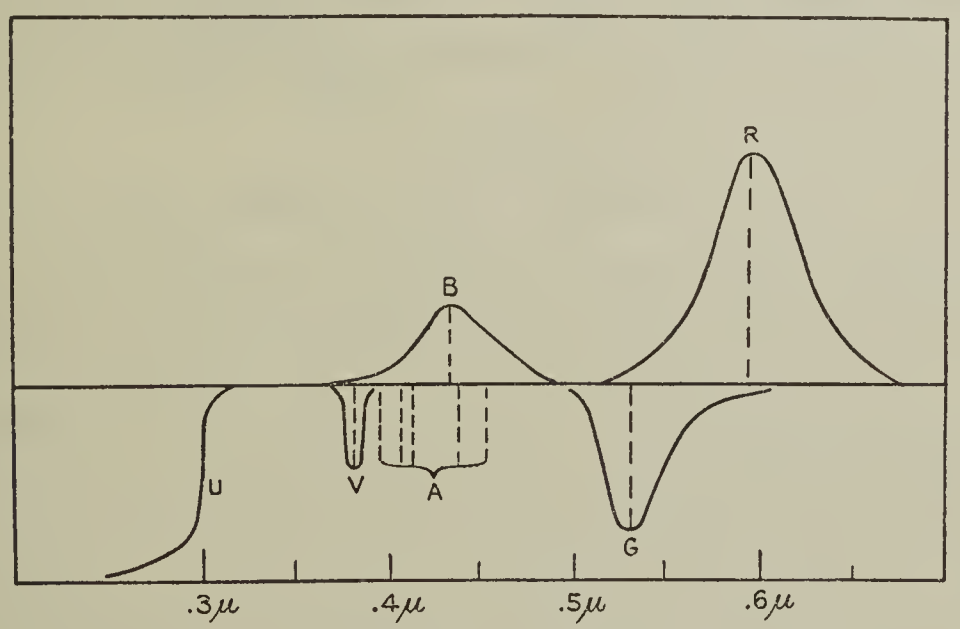


FIG. 13—Fluorescence and absorption bands in kunzite

of the crest in excellent agreement with our visual estimates. The form of the curve indicated that this complex band must also consist of close and completely overlapping components. The envelope of the band is shown graphically in figure 13, in which, however, the relative intensities of R and B are only approximately indicated.

It was found by a series of simple spectrophotometric comparisons

that when the red band (crest at 0.590μ) was equally bright for the pink and the white kunzites, the blue band (0.432μ) was about 2.33 times as bright in the fluorescence of the white kunzites as in that of the pink variety.

ABSORPTION OF KUNZITE

To determine the absorption bands associated with the fluorescence just described, observations with the spectrophotometer were made looking lengthwise through a large crystal which afforded an absorbing layer of about 5 cm. The transmitted light was distinctly purple and the measurements revealed a band which extended from 0.64μ to 0.49μ with a well-defined crest at 0.537μ. As may be seen from curve *G*, figure 13, it overlaps the violet edge of the fluorescence band *R*.

Photographs of this transmission spectrum showed also a group of narrow absorption bands (*A*, fig. 13) at 0.4019, 0.4117, 0.4170, 0.4375, and 0.4501μ. These have a width of only about 70 Ångström units. Beyond 0.4μ this thick crystal layer became rapidly opaque, making the photographic exploration difficult. By placing the crystal transversely across half of the slit of a quartz spectrograph, the transmitting layer being about 4 mm., it was possible to obtain photographs extending to 0.3μ, at which point even this thin layer became abruptly opaque, as is indicated by curve *U* in figure 13.

To determine if possible whether other bands associated with the blue fluorescence existed, a series of spectrograms through crystals of such intermediate thickness as were available were made. One of these photographs, taken through a layer of 15 mm., revealed such a band lying between 0.3750μ and 0.3875μ, with a crest at 0.380μ. This band is shown at *V*, figure 13.

Figure 13, to which reference has just been made, is intended to depict in a conventional way the fluorescence and absorption of kunzite in so far as it was determined from the foregoing experiments. In the diagram the fluorescence bands *R* and *B* are shown above the base-line and the absorption bands *G*, *A*, and *V* below that line. While the fluorescence curves give no indication of resolution, there is an intimation of systematic structure in the absorption spectrum. The group of narrow bands as we now know is suggestive of the presence of rare earths, and this suggestion is strengthened by the fact that these bands can be grouped in three sets, having the frequency interval of 18, as shown in table IV.

Subsequent measurements of two samples of kunzites made by Tanaka in course of the extensive spectrophotometric study of cathodo-luminescence which is to be described in detail in Chapters III and IV give a partial resolution of the band *R* (fig. 13). Of the

TABLE IV.—*Grouping of the narrow absorption bands of kunzite*

Set	μ	$1/\mu \times 10^3$	Δ	Departure
I	0.3800	2,632		
			$144 = 8 \times 18$	0
	.4019	2,488		
			$90 = 5 \times 18$	0
	.4170	2,398		
II	.4117	2,429		
			$143 = 8 \times 18$	−1
	.4375	2,286		
III	.4501	2,222		
			$360 = 20 \times 18$	0
	.5370	1,862		

20 components which he located in each specimen (see table XVII, Chapter IV) 11 in one and 12 in the other were identified as manganese bands, showing, as might have been surmised from the characteristic ruddy hue of the fluorescence, that that element is the chief activator of kunzite. The other components were identified as due to *samarium* and *ytterbium,* rare-earth elements having characteristic frequency intervals *of the order of 18 units.* (See Chapter III.

II. CALCITES

That calcite is luminescent has been known for many years. E. Becquerel[1] mentioned it among the numerous substances whose phosphorescence of short duration was revealed by the use of his phosphoroscope. He gave the duration as half a second.

While Stokes[2] found calcite devoid of fluorescence, von Lommel[3] described all the specimens examined by him as showing a fine red glow in the path of a beam of sunlight transmitted through the crystal.

Sohncke,[4] in his study of polarized fluorescence, found spar from Iceland active, but crystals from Cumberland, England, inactive, a fact which doubtless explains the discrepancy between the observations of Stokes and of von Lommel.

[1] E. Becquerel, La lumiere, I, p. 354, 1867.
[2] Stokes, Phil. Trans., XI, p. 516, 1852.
[3] v. Lommel, Wiedemann's Annalen, XXI, p. 422, 1884.
[4] Sohncke, Wiedemann's Annalen, LVIII, p. 425, 1896.

G. S. Schmidt[1] confirmed the experiments of Sohncke and shared his view that the luminescence is not inherent in calcite, but due to traces of foreign substances in solid solution.

Pochettino,[2] who more recently has examined many minerals under the action of cathode rays, finds calcites from some 14 localities to possess phosphorescence of considerable duration and always with the same spectral distribution. It is, however, easy, by a cursory examination of any considerable collection of calcites with the light of the iron spark, to confirm the statements of Sohncke and of Schmidt as to their varied behavior.

In an inspection by this means of the specimens available in the mineralogical laboratory of Cornell University, the present writers found many which showed the brief but vivid red glow typical of the calcites from Franklin Furnace, New Jersey; others emitted a white phosphorescence, not brilliant but of long duration, an effect apparently common among stalagmites from various localities. A few pieces were pale green, a few amethystine in the color of their fluorescence, as though by the combination of a red and a blue band. One small crystal exhibited a strikingly brilliant and persistent blue phosphorescence, which came chiefly from a small portion, not as though a foreign particle were embedded there, but rather as though some substance had gone into solution and filled a portion of the crystal bounded by growth planes which separated it from the remaining parts. Many of the calcites in this collection did not respond perceptibly to the light of the spark.[3]

It is obvious that in the luminescence of calcite we have to do with phenomena as complicated as those found in the case of the phosphorescent sulphides and like the latter dependent upon the nature and amount of the dissolved material and upon treatment by heat. In contrast to the brilliant but brief phosphorescence noted by Becquerel, Headden[4] described calcites from Joplin, Missouri, which after exposure to sunlight continued to glow with a reddish color for at least 14 hours, and others from Fort Collins, Colorado, the phosphorescence of which had a duration of several hours. The Joplin calcites were strongly thermoluminescent. Headden made a careful analysis of his material and found in addition to small amounts of Mn, Fe, and Zn, measurable quantities of the rare earths. He was inclined to attribute the phosphorescent properties to the presence of yttrium. The conclusions of Tanaka concerning the activators present in these calcites will be found in Chapter IV.

[1] Schmidt, Wiedemann's Annalen, LX, p. 740, 1897.
[2] Pochettino, Il Nuovo Cimento (5), XVIII, p. 260, 1909.
[3] Nichols, Howes and Wilber. Physical Review (2), XII, p. 351 (1918).
[4] Headden. Am. Journ. Sc. (4) XXI, p. 301 (1906).

THE EFFECT OF HEAT TREATMENT

The temperatures to which phosphorescent sulphides are subjected in the course of preparation determine their luminescent properties, as has long been known. That similar effects occur in minerals is shown by the following observations:

In a specimen from Lowville, New York, where metamorphosed rock calcite and "nail-head" crystals of calcite, presumably recrystallized from solution, occurred side by side, we found the rock calcite to give the reddish glow characteristic of the Franklin Furnace calcites, whereas the nail-head crystals were inert under photo-excitation. Since in general stalagmitic calcite does not show the red luminescence, it was thought that heat might be requisite to the production of this property. Accordingly, a piece of calcite having a faint whitish glow was heated white hot and, on cooling, the calcined tip showed the red glow. To ascertain whether a chemical impurity was also necessary to produce the phosphorescence, as suggested by the work of Crookes[1] on the yellow phosphorescence of calcium oxide containing traces of yttrium, some of Kahlbaum's reprecipitated calcium carbonate was ignited, but only the faintest white phosphorescence was obtained. A small amount of manganese chloride was added and the red phosphorescence showed at once. Some difficulty was experienced in reproducing this result, until it was found that a proper atmosphere is required during the ignition to prevent the manganese from turning black, presumably because of oxidation.

The best results were obtained by adding to 1 gram of calcium carbonate 1 c. c. of 1/50 molar manganese chloride solution, evaporating to dryness on a water-bath, adding 50 mg. of oxalic acid crystals, and grinding to a powder. The mixture was then ignited to a white heat. Ammonium chloride and sodium bicarbonate gave nearly as good results as oxalic acid, using the same weight.

The product obtained by this method glows with a reddish phosphorescence similar to that of the calcite when excited by ultraviolet light. It is, however, calcium oxide, the loss in weight being due to the loss of carbon dioxide. It deteriorates rapidly, ceasing to give any glow after standing a few weeks in the air, presumably due to the formation of calcium hydroxide.

This leads to the possibility that the phosphorescent centers are actually calcium oxide, with manganese or other oxide attached in a special manner produced by the heat treatment, and that the calcium carbonate in the calcite crystals is a matrix which holds these few scattered luminescent particles. It is conceivable that a

[1] Crookes. Proc. Roy. Soc., XLII, 115 (1887).

metamorphosed calcite could be heated to a temperature at which the carbon dioxide would slowly be driven off, leaving a small per cent of calcium oxide dissolved in the calcite.

A strong blue phosphorescence was obtained by using bismuth chloride as an activator in the place of the manganese chloride, and faint pinkish phosphorescence by employing antimony, copper, and uranium. These specimens were all strongly thermo-luminescent.

EFFECTS OF THE TEMPERATURE AT WHICH EXCITATION OCCURS

When a crystal of calcite from Franklin Furnace is excited at differing temperatures, certain changes in the character of its luminescence are noticeable. The after-glow, for example, which is ruddy at $+20°$, becomes reddish yellow and at higher temperatures a paler yellow. Before a red heat is reached phosphorescence becomes extinct, but the luminescent power returns on cooling. When excited at temperatures approaching that of liquid air the phosphorescence appears to be of a deeper, more intense red than that produced at room temperature.

The temperatures at which the color changes noted above occur seem to correspond in general to those related to the production of thermo-luminescence in calcites from Joplin, Missouri. Dr. Headden found that specimens from that locality began to glow at $+60°$, were most brilliant at about $+180°$, and were not extinct at $+200°$. We were able to confirm these observations in this regard in the case of a large crystal kindly furnished us by Professor Headden. Upon heating slowly one end of the crystal in the Bunsen flame thermo-luminescence first appeared at the hot end, then receded gradually from the flame. The luminescence was confined to a rather narrow band which moved through the crystal with the conduction of heat, showing that the effect occurred between fairly well defined limits of temperature. The appearance after several minutes was as follows: The tip of the crystal, within the flame, appeared faintly red hot; then a dark non-luminescent zone below the red heat, but above that of thermo-luminescence, appeared; then the narrow thermo-luminescent belt, very brilliant in the center and dying away more gradually toward the cooler end of the crystal. Our Franklin Furnace calcites, although strongly photo-luminescent, showed no trace of thermo-luminescence, and, strangely enough, we could not excite to phosphorescence the crystals sent us by Professor Headden either by prolonged exposure to sunlight or by the action of the iron spark, although they were of the stock examined by him in 1906, at which time they exhibited the remarkably persistent phosphorescence after solar excitation, described in his paper. The explanation of this loss in the phosphorescent properties of these calcites has not yet been found.

APPARATUS AND METHODS

The most direct method of studying the luminescence of calcite would be by observations upon the glow during excitation; but when it comes to spectrophotometric measurements this involves for photo-excitation a separation of exciting light from fluorescence, or if cathodo-excitation be used, an even more troublesome control of pressures in the vacuum-tube. The present writers chose, therefore, to use a special form of disk phosphoroscope (fig. 14) which had been devised for observations on the law of decay and to study the spectrum of phosphorescence immediately after the cessation of excitation. This instrument consists essentially of a drum about 8 cm. in diameter, mounted upon a vertical shaft and driven by a small electric motor. It could be belted direct to the motor from any one of three pulleys at the base of the shaft, or, for low speeds, to a large pulley driven by worm-gearing on the motor-shafts. Thus the very great range of speeds necessary in phosphoroscopic measurements was readily obtained.

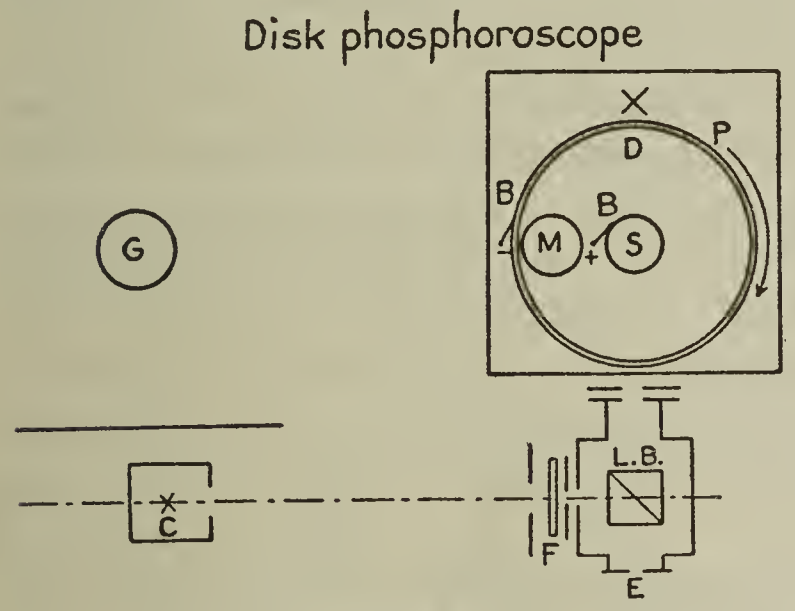


FIG. 14—The disk phosphoroscope

For the indication of speeds, a brass disk was mounted on the shaft of the phosphoroscope below the drum. This passed between the poles of a little electro-magnet. Brushes on the periphery of the disk and on the shaft conveyed the current generated by this disk dynamo to the circuit of a d'Arsonval mirror galvanometer. Adjustments of the resistance of the galvanometer circuit afforded deflections through the same range for the various speeds employed and enabled us to follow all changes in the rotation of the phosphoroscope, regardless of the slip of the belt or of fluctuations in the current-supply of the motor. Constancy of the field of the disk dynamo was secured by the use of storage-cells and precautions were taken to eliminate thermal E. M. F.'s at the brushes. The phosphorescent material, in powdered form, was mixed with white zapon varnish and applied with a brush to the outside of a brass collar which fitted snugly over the slightly tapered drum of the phosphoroscope. A number of these collars, which were readily interchangeable, were provided to facilitate the examination of one substance after another.

Excitation was by means of an iron spark actuated by the convenient form of transformer devised for this purpose by Mr. W.

S. Andrews,[1] or sometimes by means of a mercury arc in quartz, the tube of which was brought as close to the drum of the phosphoroscope as possible.

With the simple instrument just described, exceedingly interesting and instructive observations of phosphorescence having a visible range between 0.01 second and 3 or 4 seconds may be made. The color-changes in the phosphorescence of bodies whose spectra have two or more bands which differ in wave-length and persistence are beautiful and most striking.

To determine more exactly the effects of temperature, the disk of the phosphoroscope was heated by means of a circle of minute gas jets. Figure 15 shows the arrangement as seen from below, where *JJ* are the jets, and *S* the spark-gap for excitation of the layer of calcite upon the rim of the drum. The temperature of the ring on which the powdered calcite was mounted was measured by means of a Pt-Cu thermo-junction *T*, which could be inserted in a drill-hole in the metal of the ring.

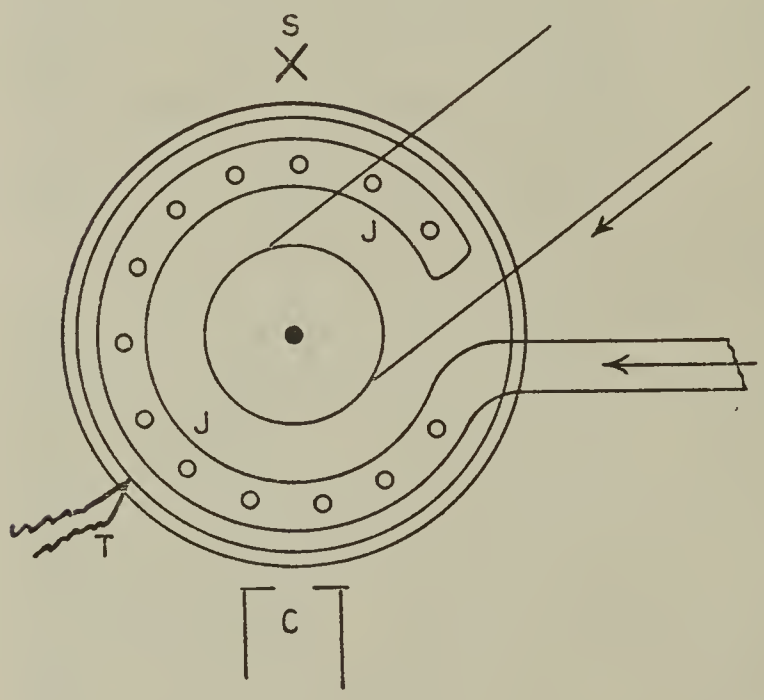


FIG. 15—Disk phosphoroscope from below, showing heating ring and thermo-junction

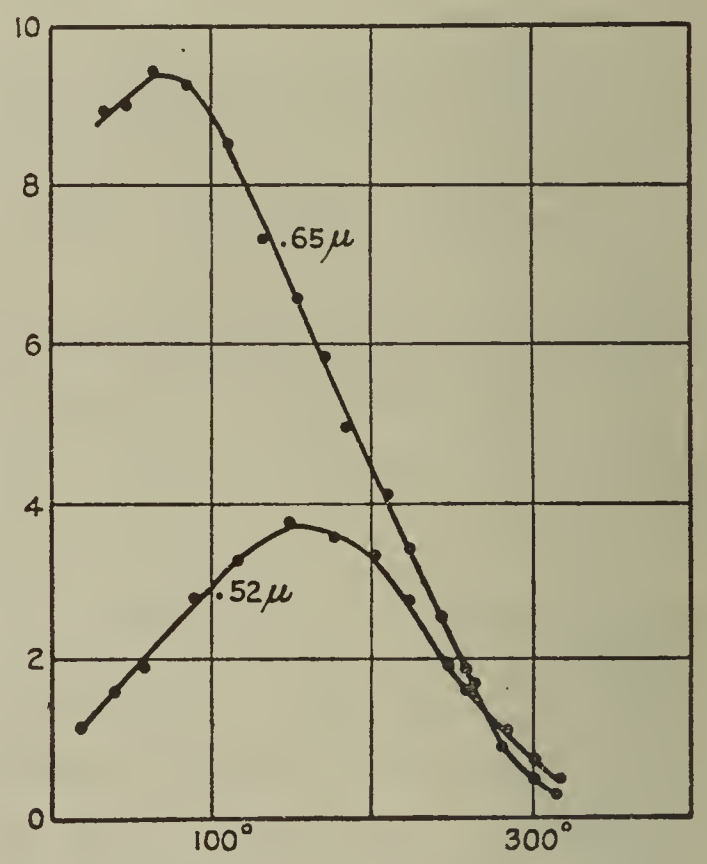


FIG. 16—Effect of temperature on the phosphorescence of calcite

The phosphoroscope was driven at a constant speed and the brightness of the coating at various temperatures between +20° C. and +350° was measured by means of a Lummer-Brodhun spectrophotometer, one collimator of which was directed toward the coating of the phosphorescent calcite at *C*. The other collimator was illuminated by the comparison lamp. Slit-widths were maintained equal and constant, and measurements were made by moving the

[1]Andrews. General Electric Review, XIX, 317-319, 1916.

comparison lamp along a photometer bar. Readings were made in the red of the spectrum (0.65μ) and in the green (0.52μ).

Accurate determinations by this method are difficult, since they involve constant intensity of excitation and constant speed of the phosphoroscope throughout the run. Both conditions were hard to maintain with our apparatus. Fair control of the speed could be had only by continual attention to the lubrication, particularly at the higher temperatures, where castor oil had to be substituted for the more volatile lubricants. This trouble could have been completely overcome by suitable reconstruction of the phosphoroscope, but it seemed hardly worth while on account of the uncertain behavior of the iron spark. This source of excitation is altogether unsatisfactory where intense and really constant intensities are demanded. We have not as yet found an adequate substitute, however, for strong excitation by ultra-violet radiation.

At the higher temperatures the heated air greatly interfered with the action of the spark. To obviate this, a quartz window was mounted between the disks and the spark, but we were greatly surprised to find that the excitation was reduced to a small fraction of its former intensity.

It appears that the luminescence of these calcites is chiefly produced by rays which are of shorter wave-length than those transmitted by quartz. This almost precluded the use of a mercury arc in quartz for these observations, although we did make several sets of spectrophotometric measurements with this source by way of a check.

The curves in figure 16 show the variations in the red and green throughout the range of temperatures mentioned above. Ordinates are intensities, referred to that of the corresponding region in the spectrum of the comparison light, and the readings are numerically comparable only if reduced to terms of energy. For the present purpose, which is to depict the relative effects of temperature, the curves in their present form will suffice. It will be noted that in both of these regions the brightness increases with the temperature. The red, however, reaches a maximum at about 70°, whereas the green continues to rise to about 160°. After passing the maximum, the fall of both curves is continuous and rapid, and they approach extinction, *i. e.*, become too feeble for measurement, at about 350°.

The marked change in color is indicated by the fact that whereas if at 20° the region at 0.52μ be made as bright as the corresponding region in the spectrum of the comparison source, the red would be about 50 times as bright as the red of the comparison, while above 250° the relative brightnesses become nearly equal. At these higher temperatures, indeed, the distribution of intensities in the spectrum

of the phosphorescence differs but little from that of a tungsten lamp up to about 0.5μ. Its spectrum extends but little beyond that wavelength toward the violet, however, and the color is accordingly a fine luminous yellow.

SPECTROPHOTOMETRY OF THE PHOSPHORESCENCE AT +20° AND +200°

The differing effects of temperature upon the two regions of the spectrum, as just described, are indicative of the presence of more than one band in the phosphorescence of these calcites. The components of the spectrum overlap, however, to such an extent as to be indistinguishable by spectroscopic inspection. We undertook, therefore, a detailed spectrophotometric study, making measurements every 50 Ångströms from 0.66μ to 0.50μ.

It was easier to ascertain the deviations from constancy of the phosphorescent surface, due to irregularities in the iron spark or fluctuations in the speed of the disk, than it would have been to control these conditions throughout an entire spectrophotometric experiment. To this end a photometer was mounted so as to follow the fluctuations. The arrangement of the apparatus is indicated in figure 17.

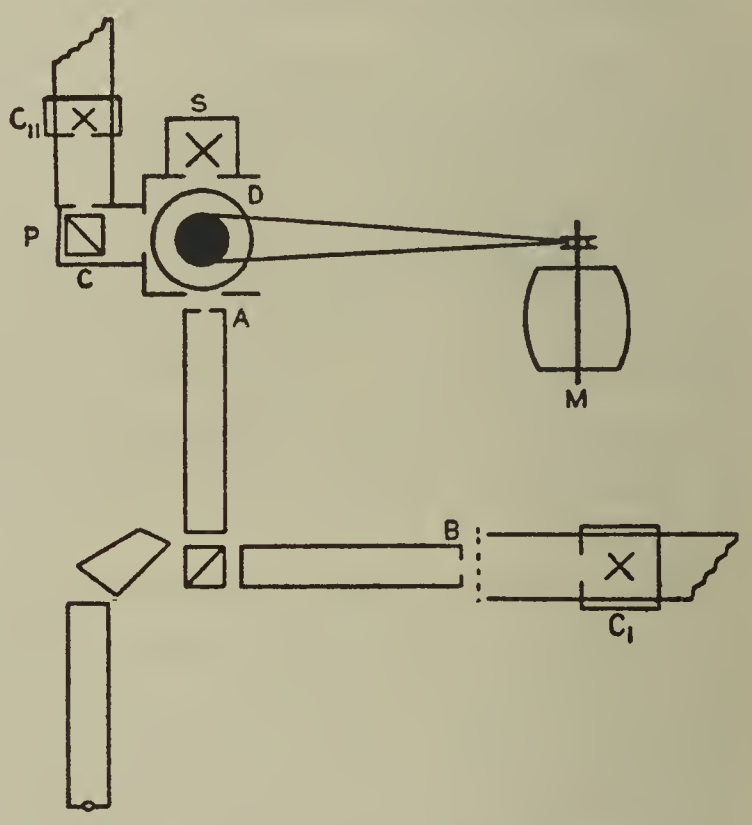


FIG. 17—Disk phosphoroscope, spectrophotometer, and photometer

The disk phosphoroscope *D*, already described, is driven by the motor *M*. The spark-gap is within the inclosure *S*. The collimator *A* of the spectrophotometer receives light from the phosphorescent ring on the disk, 180° from the point of excitation. The photometer *P* is so placed as to permit observations of the brightness of the ring at a point 90° beyond *A*. The comparison lamps C_I and C_{II} mounted on photometer bars, as shown, serve respectively the collimator *B* and the photometer. The comparison lamps are similar 6-volt tungsten lamps in multiple on a circuit supplied by a suitable storage battery.

The method requires two observers, one at the eyepiece of the spectrophotometer, the other at the photometer. The latter follows the fluctuations of the phosphorescence and records its brightness at the instant when each spectrophotometric setting is made. It was

thus possible to eliminate, with a fair degree of accuracy, all errors due to changes in the excitation or speed.

Spectrophotometric measurements were made with this apparatus with the disk at +20° and at +200°. The results are shown in the two curves in figure 18 in which ordinates are ϕ_λ/C, where ϕ^λ is the intensity of the phosphorescence spectrum at wave-length λ and C is the intensity of the spectrum of the comparison lamp at the same wave-length. Abscissæ are frequencies, or $1/\mu \times 10^3$. The lower curve in the diagram is for 20° and the upper curve for 200°.

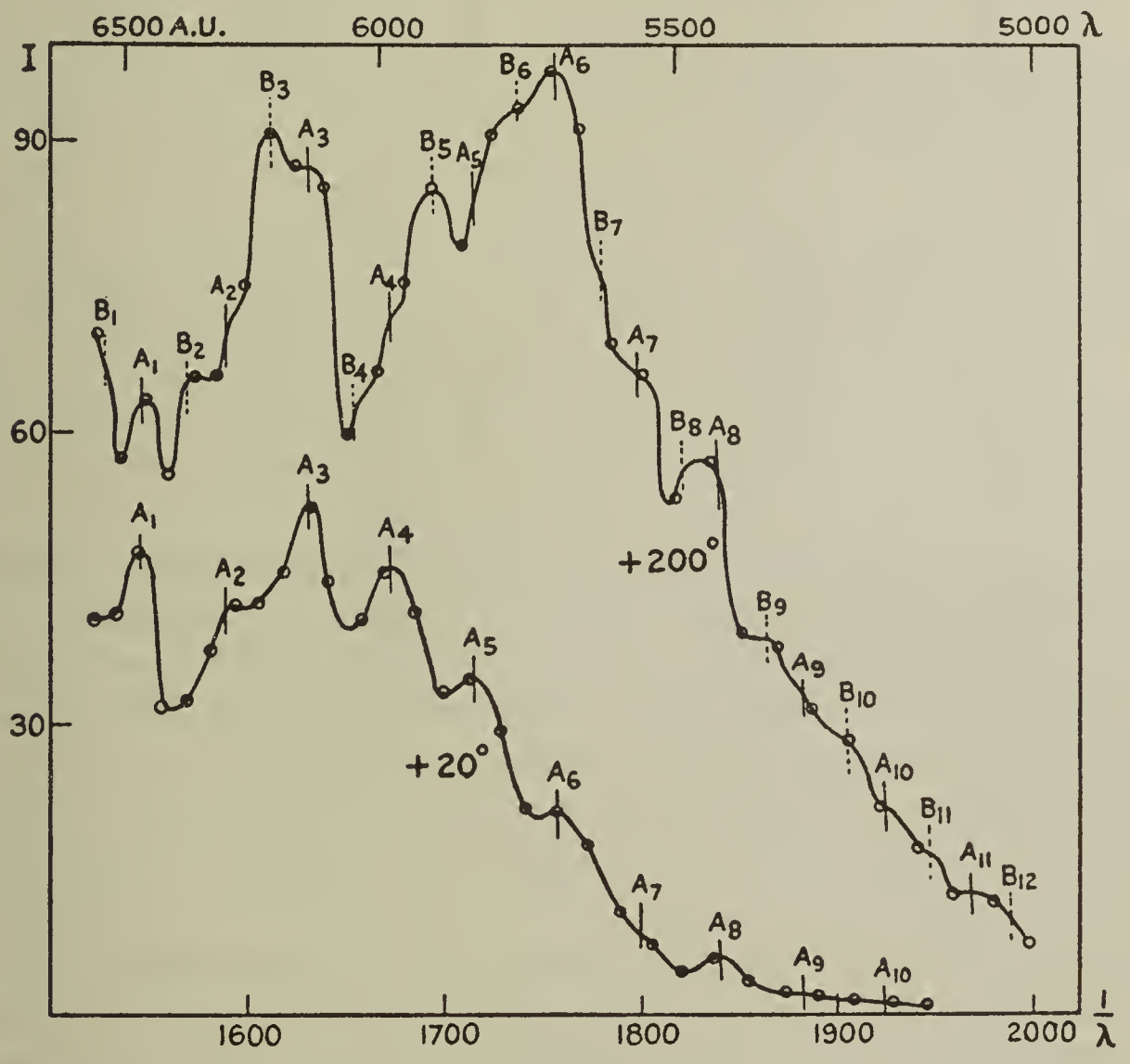


FIG. 18—Phosphorescence of calcite at 20° and at 200° C. showing the overlapping and semisubmerged crests

The curve for +20° shows the phosphorescence spectrum to be complex, consisting of numerous overlapping components grouped about the main crest at 0.6131μ ($1/\mu \times 10^3 = 1{,}631$). If we assume that the components form a set with equal frequency differences, and take 42 units as the approximate interval, assigning one member of the set to the peak of the principal crest as above, we get the set of components shown in table V:

These frequencies coincide in position with the subordinate crests that are visible as ripples in the curve in figure 18. Their positions are indicated by the short vertical lines marked *A* which cross the curve.

TABLE V.—*Bands in the Franklin Furnace calcite*

Band	μ	$1/\mu \times 10^3$	Band	μ	$1/\mu \times 10^3$
SET A (INTERVAL 42)					
A_1	0.6464	1,547	A_7	0.5559	1,799
A_2	.6293	1,589	A_8	.5432	1,841
A_3	.6131	1,631	A_9	.5311	1,883
A_4	.5977	1,673	A_{10}	.5195	1,925
A_5	.5831	1,715	A_{11}	.5084	1,967
A_6	.5692	1,757			
SET B (INTERVAL 42)					
B_1	0.6545	1,528	B_7	0.5618	1,780
B_2	.6369	1,570	B_8	.5488	1,822
B_3	.6203	1,612	B_9	.5365	1,864
B_4	.6046	1,654	B_{10}	.5247	1,906
B_5	.5896	1,696	B_{11}	.5133	1,948
B_6	.5754	1,738	B_{12}	.5025	1,990

There are suggestions of a secondary or accompanying series, but the indications of it in the curve for 20° are not sufficient to establish its position or interval. In the curve for 200°, however, which is the upper curve in figure 18, this secondary series (*B*) is strongly developed and becomes quite as prominent as series *A*. The strongest crest is now found at 0.5692μ ($1/\mu \times 10^3 = 1{,}757$) and is broadened as if due to the presence of an unresolved doublet. Its edge toward the violet coincides in position with A_6 in the 20° curve. Its edge toward the red may be regarded as due to the outcropping of a member of series *B*, the location and interval of which can be pretty definitely established from the crests B_3 and B_5. This series in both curves is indicated by short broken vertical lines (B_2, B_3, etc.) Its interval is also approximately 42 units of frequency.

The structure of the spectrum of this calcite resembles that of the phosphorescent sulphides, which, as has been shown in a foregoing chapter, is made up of one or more series of overlapping components. The luminescence of the calcite, however, differs in at least one important respect from that of the sulphides. The light from the sulphides, as is well known, is quenched by exposure to infra-red. The glow of the calcite is not appreciably affected by such radiation either during or after excitation. Of this we assured ourselves by careful observations.

To determine whether the Franklin Furnace calcite which has been subjected to cathodo-bombardment acquires, even temporarily, the power of photo-phosphorescence, a crystal was mounted in the V-shaped cathode-ray tube already described (fig. 11). A quartz lens was cemented over the open end of the tube, in place of the ground-glass plug. The crystal glowed in the usual manner after excitation by the cathode rays.

Exposure to radiation from an iron spark mounted just above the quartz window produced the same brief red after-glow, whether applied before, during, or after cathodo-excitation. The two effects appeared to be quite independent and could be produced simultaneously and superimposed.

It was in connection with these experiments that the following tentative observations on the effect of low temperatures were made. The knee of the V-tube was submerged in liquid air and cathodo-excitation was used. The luminescence seemed to the eye redder than at room temperature and very bright. The increase in intensity may, however, have been due to improvement in the vacuum due to cooling and a consequent change in the cathode discharge.

Photo-excitation gave the same brief ruddy after-glow as at room temperature, seemingly of a deeper red. No notable change in duration was observed. No quantitative measurements of color, intensity, or duration were made at these temperatures.

As to the frequency-interval which characterizes the luminescence spectrum of calcite the following points may be noted:

(1) *The frequency interval is the same at 20° and at 200° and the same sets occur.* Thus the spectra at these two temperatures are *essentially identical* and the changes of color with temperature are produced by variations in the brightness of the various components without perceptible shift.

(2) The frequency interval is the same as that found in the fluorescence spectrum of the kunzites studied by Tanaka for the bands assigned by him to manganese, and sets *A* and *B* in our measurement of the Franklin Furnace calcite (table V) are identical with the corresponding sets of his determination. (See Chapter IV.)

The spectra of the kunzites taken as a whole, and of this calcite, can not be said to be essentially identical, because, according to Tanaka, there are at least three activators (manganese, samarium, and ytterbium) in the kunzites; but so far as the bands due to a single activator (manganese) are concerned the indications are of essential identity.

This point was established for bismuth also in our studies of the phosphorescent sulphides, and later in numerous cases for manganese in the work of Tanaka to be described in Chapter III.

The evidences of a systematic intimate structure in fluorescence spectra brought out in the experiments described in this and the foregoing chapter were the starting-point and incentive for the more extended and far-reaching investigations of Tanaka which form the subject-matter of Chapters III and IV of the present monograph.

CHAPTER III

THE CATHODO-LUMINESCENCE OF SOLID SOLUTIONS OF FORTY-TWO METALS

[Describing Experiments by T. Tanaka, 1921–1923]

The evidence of the complex structure of luminescence spectra afforded by the measurements described in Chapters I and II formed the starting-point of an extended and systematic investigation subsequently carried out by Professor Tutoni Tanaka in the Physical Laboratory of Cornell University (1921-1923). His method and results are given in somewhat greater detail in the present chapter than was done in the original paper.[1]

I. METHOD OF INVESTIGATION

The method of excitation adopted in the present investigation was by cathode rays obtained in a vacuum-tube carrying currents of about 0.4 milliampere. The discharge potential, which was measured with a spark-gap voltmeter, was found to be about 4,000 volts in most cases. The currents were produced by a large Holtz machine with two plates, and a two-stage oil-pump was used to exhaust the air from the tube. The electric machine was driven by an alternating-current motor at full speed, the strength of the current being adjusted by alcohol resistance. The vacuum-pump was rotated by a direct-current motor attached to a slide-rheostat, by which the speed of rotation could be adjusted.

To achieve success it was extremely important to obtain a steady current. Therefore, as far as possible, all contacts were soldered, all surfaces of conductors were coated with sealing-wax or paraffin, and all wires, besides being as large as was convenient, were inserted into glass tubes. In this way quite steady currents were obtained, so that the readings of a D'Arsonval galvanometer inserted between the alcohol resistance and the ground showed only a few minor oscillations in the course of 30 or 40 minutes. In most cases it was necessary to keep the pump slowly rotating, otherwise the pressure in the vacuum-tube soon increased, a phenomenon probably due to gases produced from the luminescent substance by the bombardment of cathode rays. In consequence of this, the vacuum-tube slowly hardened, so that in the course of 30 or 40 minutes there was a gradual decrease of current and increase of discharge potential. Such slow

[1] T. Tanaka. Jour. Opt. Soc. Am., VIII, 287-318, 1924.

changes, amounting only to a few per cent, have little injurious effect on the present investigation.

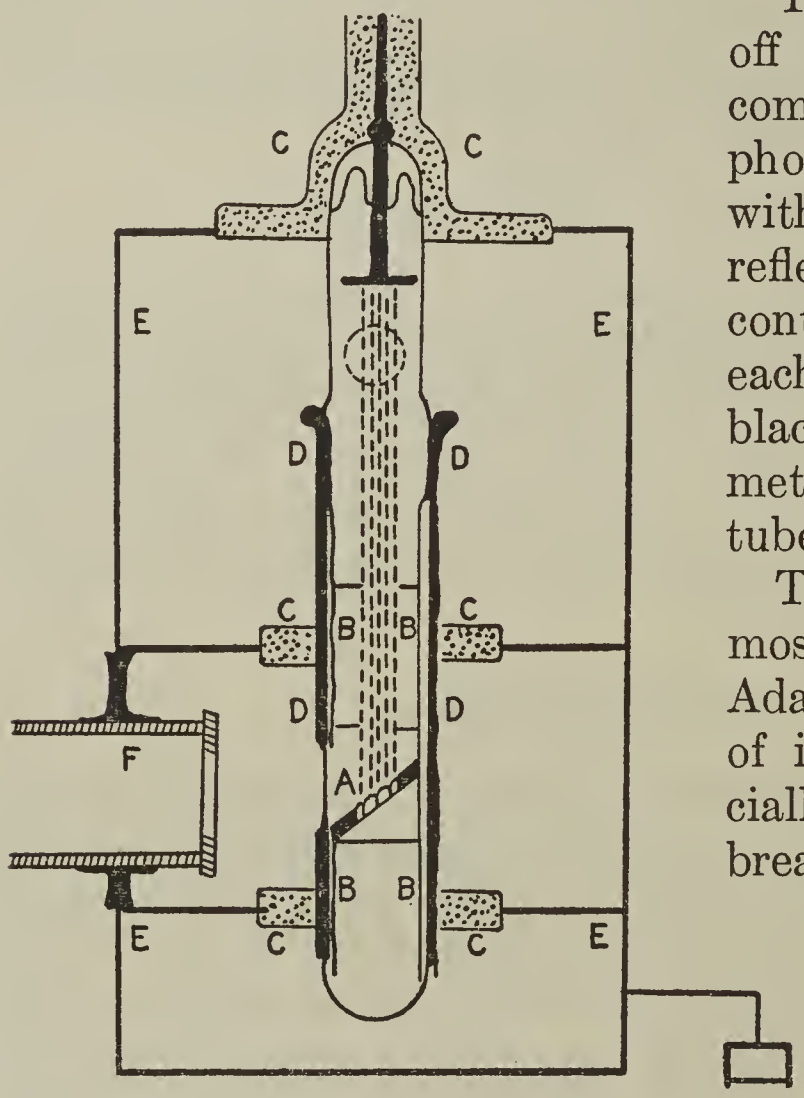


FIG. 19—Apparatus used by Tanaka

The stray light, also, was cut off with the greatest care. The compartments for the spectrophotometer, the comparison lamp with its magnesium carbonate reflector, and for the metal case containing the vacuum-tube, were each tightly inclosed by thick black paper. One part of the metal case containing the vacuum-tube is shown in figure 19.

The spectrophotometer used in most of the work was made by Adam Hilger. Several verifications of its accuracy were made, especially in respect to the effect of the breadths of the ocular slit and of the slits of both collimators, and the scale was frequently calibrated by lines of the light from a mercury arc lamp.

The comparison light was furnished by a miniature tungsten lamp of 3.8 volts, whose current was adjusted by a milliammeter and a rheostat inserted in the circuit. Each lamp was thrown away after being used about 10 hours. For the energy distribution of this comparison light, Coblentz's result was used as an approximate datum.[1]

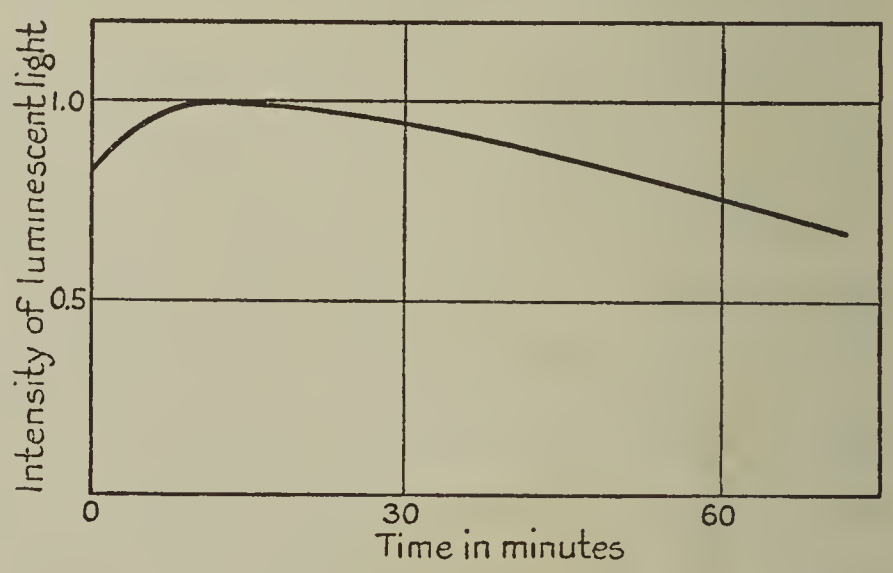


FIG. 20—Intensity of luminescent light against time

The readings of the spectrophotometer were generally taken at intervals of 20 Å. U. Some faint luminescence bands due to the glass wall of the container of the sample were often perceptible, especially when the luminescence of the sample was faint. The crests of these bands were at 4,702 and 4,268 Å. U. for the tube that was used the longest.

[1] W. W. Coblentz. Bull. Bur. St. 14, p. 115-131 (1917-18).

It was easy to distinguish them from bands due to the sample, by reason of their constant occurrence.

Before beginning the investigation proper, it seemed necessary to examine spectro-photometrically the variation of the intensity of the luminescent light for a definite wave-length of each substance. Repeated experiments were made, readings being taken every minute. Figure 20 shows the approximate intensity of the luminescent light of λ=5,977 Å. U., emitted by a calcite from Colorado, for about an hour after the current became stationary. This wave-length corresponds to the crest of a band appearing prominently in that crystal. From this it can be seen that, except for 7 or 8 minutes at the beginning, the conditions for 30 or 40 minutes are suitable for finding the positions of narrow bands, the object of the later experiments. The variations of intensity shown in these preliminary experiments are to be attributed to variations in the samples themselves, due to the cathode-ray bombardment. For most substances, the rate of decrease was found to be somewhat larger than that shown in figure 20.

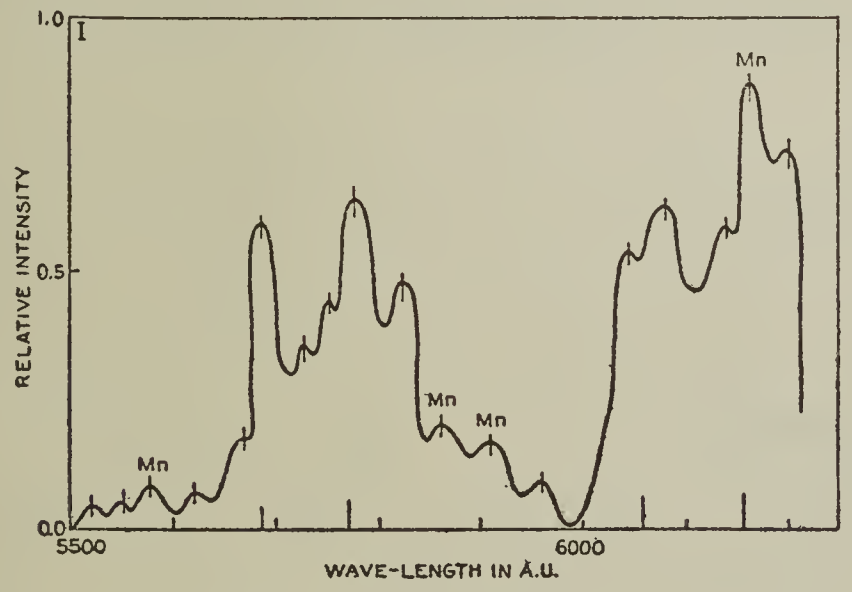


FIG. 21—Relative intensity against wave-length. I

The luminescence spectra obtained in the present investigation can be classified as follows: Type I, the so-called line spectra; type II, spectra consisting of one or several groups of bands, each of which appears as a single band; type III, spectra for which the envelope of the spectrum curve has no distinct summit, and the luminescent color is whitish. Figures 21 to 23 show examples of these three types.

Figure 21 is the spectrum curve of the luminescence of a mixture of calcium carbonate and samarium oxide (proportion of atoms 125 : 1, calcination accomplished by heating to red heat for about half an hour). When this spectrum was viewed through a telescope with an eye-piece inserted, it appeared to consist of four separated, fairly sharp bands, the positions of which are shown by the

vertical lines at the bottom of the figure. The calcium carbonate used had been determined beforehand to contain traces of manganese.

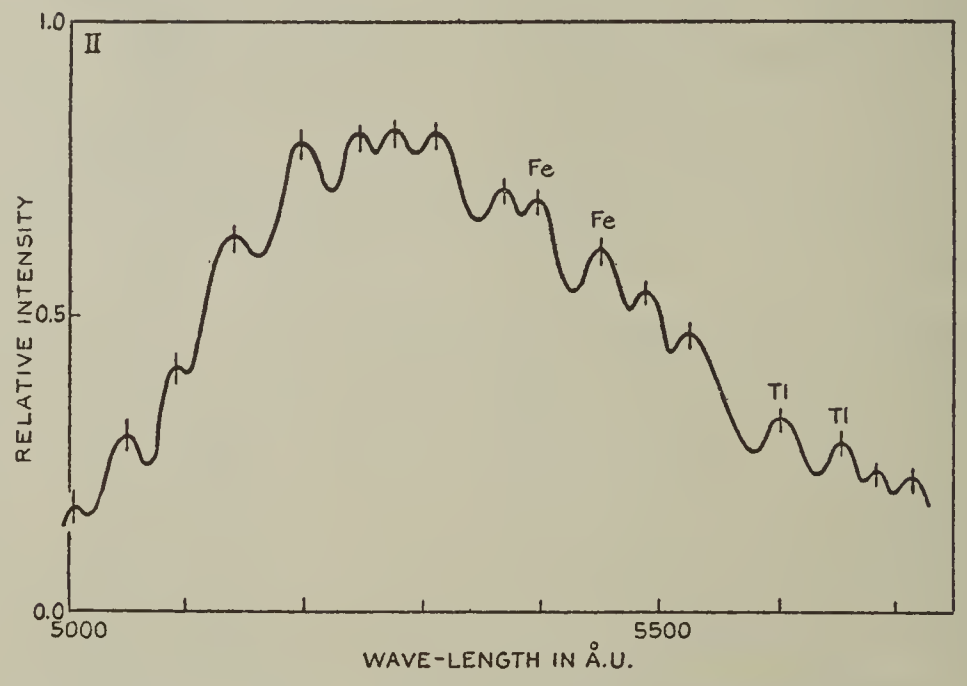


Fig. 22—Relative intensity against wave-length. II

Figure 22 is the spectrum curve of the luminescence of a mixture of zinc silicate and manganese oxide (Andrews's synthetic willemite), of which the method of preparation will be found in section VII of this chapter.

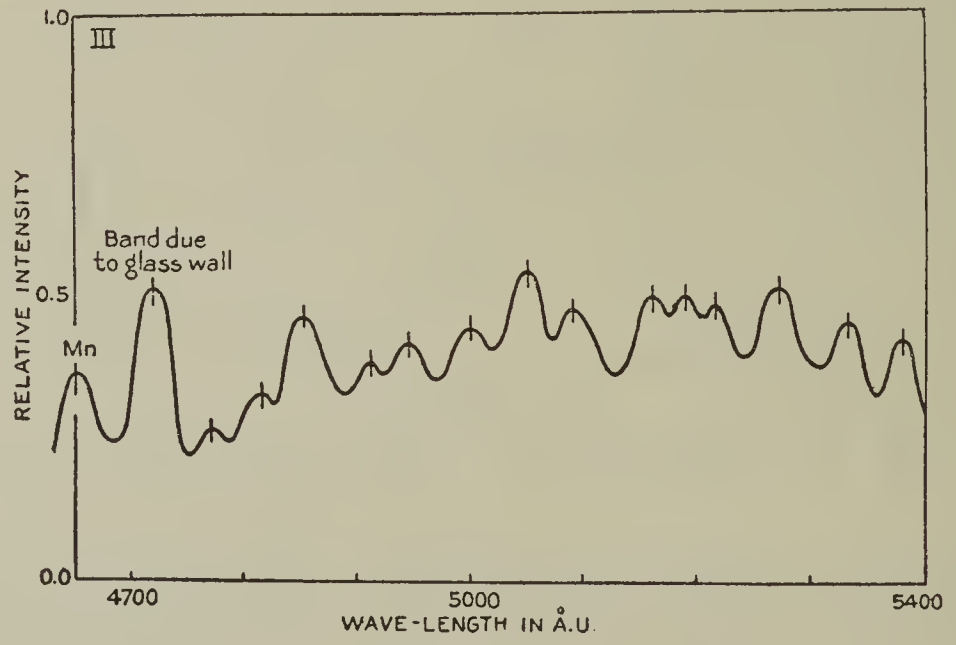


Fig. 23—Relative intensity against wave-length. III

Figure 23 is the spectrum curve of the luminescence of a mixture of calcium fluoride and molybdic oxide (proportion of atoms 250 : 1, calcination accomplished by heating to red heat for about half an hour). In this case one band due to the glass wall of the tube (not the same tube as that previously mentioned) occurred.

The points of observation were purposely not plotted, because each spectrum curve drawn expresses the results of at least ten series of observations.

II. SOLID SOLUTIONS WITH MANGANESE AND WITH COPPER AS THEIR ACTIVE SUBSTANCES

(1) *Calcium sulphate with manganese as the active metal*—This solution consisted of calcium sulphate containing about 0.10 per cent of manganese sulphate. It was heated to 690°, and showed a bright-green luminescence, with its maximum brightness at about $\lambda=0.505\mu$, a wave-length coinciding approximately with the result of Bruninghaus.[1] Upon drawing many spectrum curves, it was found that the spectra consist of four sets of overlapping bands, each being spaced equally in frequency units. (In accordance with the usual notation, frequency will be expressed in terms of $1/\mu \times 10^3$ or $1/\text{Å. U.} \times 10^7$ hereafter.) In this notation, two of the above-mentioned sets have 34 as their interval and the other two have 42. Part 11 in table VIII shows the wave-lengths and frequencies for these sets. The sets III and IV in that table coincide with those found by Nichols, Howes and Wilber in calcite and quicklime, using a different method of excitation,[2] from which it would be expected that these substances and the present solution have a common luminescent agent. Series I and II are new. Generally speaking, each spectrum of the present solution contains bands belonging to each of these sets; but a long bombardment by cathode rays causes the number of bands belonging to sets III and IV to decrease, and the number of those belonging to sets I and II to increase, which indicates that the bombardment produces a change in the physical condition of the substance. This change is semipermanent and is not reversed by several hours' rest. Several experiments on this phenomenon were performed, in the region of 0.545μ—0.475μ. At the beginning of the bombardment, 8 bands belonging to I and II and 6 belonging to III and IV were present. After a time, 2 new bands of I and II appeared, and 2 of III and IV disappeared. Later, 2 more new bands of I and II appeared, while 3 of III and IV disappeared. Lastly, 2 more new bands of I and II appeared, and all of III and IV disappeared. Upon introducing fresh powder, about an equal number of bands belonging to the two groups were again found. This shows that the condition of the substance is gradually changing in the course of bombardment, a fact that makes the study quite difficult. If, as it seems, there is a certain condition of the substance favorable to the appearance of bands of a given set, it is quite natural that Nichols, Howes, and Wilber, using a different method of excitation, should have observed only the existence of sets III and IV.

[1] M. L. Bruninghaus. C. R. CXLIV, p. 1040 (1907). (Note that Bruninghaus and some other French physicists speak of cathodo-luminescence as "phosphorescence.")

[2] E. L. Nichols, H. L. Howes, and D. T. Wilber. Phys. Rev. (2), XII, p. 351-367 (1918). H. L. Howes. Phys. Rev. (2), XVII, p. 469-474 (1921).

(2) *Calcium carbonate with manganese as the active metal*[1]—The resolution of the luminescence band showed the existence of four sets of bands, coinciding with those discussed under (1). But the luminescence was orange instead of green, and had its maximum brightness at about 0.595μ, a value approximately coinciding with that found by Bruninghaus. Bands belonging to the two groups of sets appear and disappear in the same way as has been previously described.

(3) *Calcium phosphate with manganese as the active metal*[1]—This substance showed a very bright yellow luminescence, with a fairly large fatigue of the luminescent power. The maximum brightness occurred at about 0.554μ, differing from the value of 0.633μ observed by Bruninghaus. The difference may be due to differences in the concentration or in the calcination temperature. The bands belonged to the same four sets which have been previously discussed.

(4) *Zinc sulphate with manganese as the active metal*—This substance showed a red luminescence having its maximum brightness at about 0.647μ. In this case the luminescence spectrum resolved itself into component bands constituting eight sets. Four of these were the sets I, II, III, IV, previously described, and the other four could be derived from the four normal sets by displacing each member thereof by 2.5 frequency-units toward the red end. Furthermore, the bands of the normal sets occurred only in a comparatively early stage of the bombardment. At first, this anomaly was considered due to something wrong in the apparatus; hence the experiment was repeated 30 times, using two different spectrophotometers, one of which was made by Adam Hilger, and by which the wavelengths could be read accurately to at least 2 or 3 Å. U. The results of all these experiments agreed.

Members of the groups I, II, and III, IV, appeared and disappeared in the same manner for these anomalous sets as for the normal series. For instance, in one experiment the results were as follows: First, no bands of I, II; 7 bands of III, IV. Second, same as first. Third, 3 bands of I, II; 5 bands of III, IV. Fourth, 5 new bands of I, II; only 1 band of III, IV remained. No further change was observed.

A subsequent study of zinc silicate mixed with manganese oxide (Andrews's synthetic willemite; see section VII of this chapter) failed to show any trace of these anomalous sets; perhaps they are peculiar to zinc sulphate.

(5) *Magnesium sulphate with manganese as the active metal*—This solution consisted of magnesium sulphate containing about 1.3 per cent of manganese sulphate. Upon being heated to 690° it

[1] The method of preparation was unknown

showed a red luminescence with a maximum brightness occurring at about 0.631μ. The component bands belonged to the previously described normal sets.

(6) *Ammonium alum with manganese as the active metal*—This solution consisted of ammonium alum containing about 0.11 per cent of manganese carbonate. Upon being heated to 690° it showed a faint red luminescence, the component bands of which belonged to the four normal sets.

(7) *Calcium sulphate with copper as the active metal*—This showed a luminescence of medium intensity, resolving itself into bands constituting two series with a common interval of 17.0. These sets are shown in part 15 of table VII.

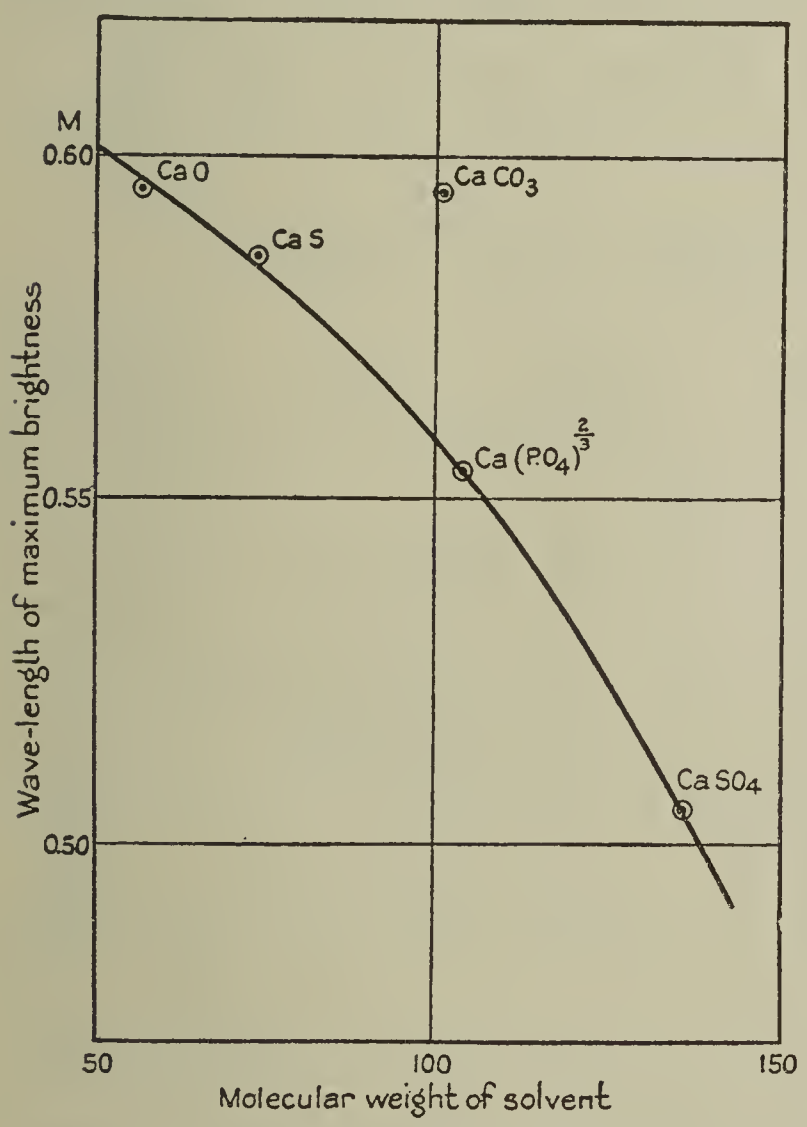


FIG. 24—Maximum brightness against molecular weight of solvent

(8) *Magnesium sulphate with copper as the active metal*—This showed a rather faint red luminescence, presenting an anomalous case similar to that discussed under (4). Besides the two normal sets found in the preceding case, two other sets appeared, which could be derived from the normal sets by displacing each member thereof by two frequency-units toward the violet end.

So far as found in the present investigation, in the case of calcium salts with manganese as the active metal, the position of the maximum brightness of luminescence varies regularly with the molecular weight of the salt, as shown in figure 24. The points for CaO and CaS were determined from a study to be later described. It is interesting to note that calcium carbonate acts similarly to calcium oxide, probably in consequence of the liberation of carbon dioxide by the cathode-ray bombardment. Differences of concentration and of calcination temperature, which might occur in different samples, do not seem to affect this result.

SUMMARY OF SECTION II

(1) All the solid solutions with manganese or copper as their active metals show luminescence spectra which can be resolved into series of component bands characteristic of manganese or copper respectively.

(2) The solvents determine the position of the maximum brightness, and in a few cases produce a small modification in the positions of the bands.

III. LENARD AND KLATT'S SULPHIDES

The numerous sulphides made by Lenard and Klatt afford a promising object of study on many accounts. First, we can rely on a high degree of purification in the substance; second, the intensity of the luminescence of the active metal is so great as to make that of possible impurities inconsiderable; third, there are a sufficient number of these sulphides to offer a chance for the discovery of important relations. Moreover, every spectrum curve obtained by the present author showed subordinate crests much more distinct than those obtained by Howes (who used a different method of excitation).

The list in table VI gives the active metal, base, flux, color of luminescence, etc., of the 22 Lenard and Klatt sulphides studied.

TABLE VI—*Lenard and Klatt sulphides used in this investigation*

Active metal	Base	Flux	L. and K. No.	Color of luminescence	Approx. maximum
Copper[1,2,3] (part 15, table VIII)[4]	SrS	CaF_2	2	Bright green	0.53
		Na_2SO_4	8	Do	0.53
		$MgHPO_4$	17	Do	0.53
		$K_2B_6O_{10}$	23	Do	0.53
	BaS	NaF	18	Greenish yellow	0.57
		NaCl	24	Yellow	0.57
		$Na_2B_4O_7$	33	Orange yellow	0.57
	CaS	$Li_2SO_4.CaF_2$	3	Bright blue	0.48
		Li_2SO_4	32	Do	0.48
Lead (part 41, table VIII)	SrS	$Na_2SO_4.NaF$	15	Yellowish green	0.535
		NaF	25	Green	0.535
	BaS	Na_2SO_4	26	Yellow	0.558
	CaS	$Na_2SO_4.NaF$	29	Bluish green	0.51
Bismuth[5,6] (part 42, table VIII)	SrS	Na_2SO_4	13	Green	0.52
	BaS	$Na_2B_4O_7$	16	Yellow with orange tint.	0.57
		$K_2B_6O_{10}$	20	Yellowish orange	0.57
	CaS	$Li_2SO_4.Na_2SO_4.$ $CaF_2.Na_2B_4O_7$	12	Deep blue	0.47
Manganese[1,2] (part 11, table VIII)	SrS	Na_2SO_4	6	Yellowish green	0.535
	CaS	$Na_2SO_4.CaF_2$	5	Yellowish orange	0.585
Silver (part 25, table VIII)	SrS	$Li_2SO_4.Li_2CO_3$	28	Purple	Indef.
		Na_2SO_4	30	Green	Indef.
Antimony (part 26, table VIII	CaS	$Na_2SO_4.NaF$	27	Blue	0.485
Zinc[7]	SrS	CaF_2	7	Green	0.55

[1] The normal sets for copper and manganese are the same as those obtained in section II.

[2] BaS with copper as the active metal showed, besides the two normal series of copper, two sets differing from the normal ones by $\Delta(1/\lambda) = 3.0$. SrS with manganese, as the active metal

The characteristics noted in table VI are not always in agreement with those obtained by Lenard and Klatt themselves.[1] There are probably several causes for the deviations. One is the difference in methods of excitation; a second is the possible gradual changes in the course of several years in the properties of such highly luminescent substances, artificially made; a third is that in this investigation observation was restricted to the region in which exact measurements were possible, and that the maximum brightness recorded may often be that for this region, without being a maximum for the whole spectrum.

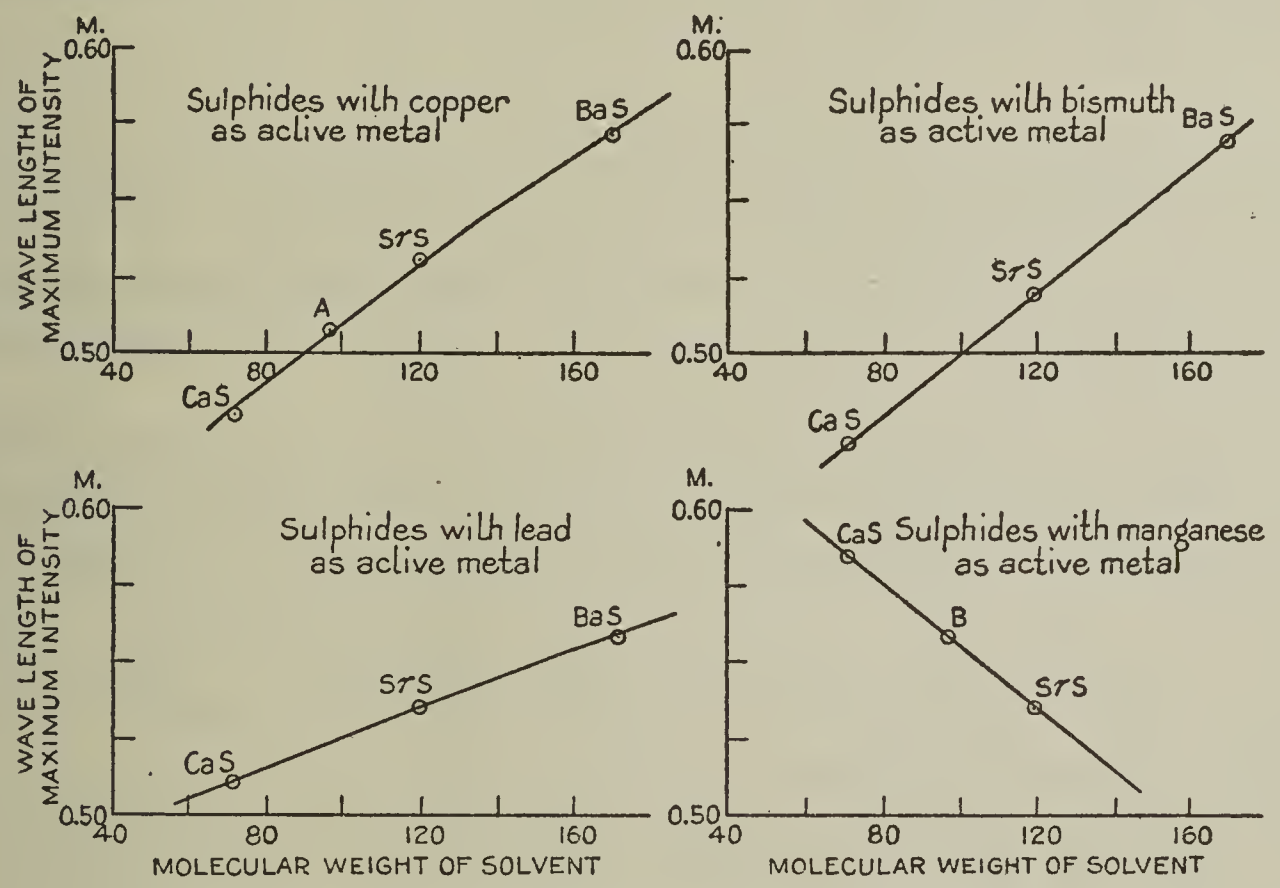


FIG. 25—Maximum intensity against molecular weight of solvent for sulphides activated by copper, lead, bismuth and manganese

The position of the maxima of brightness seems to change with some regularity with the atomic weight of the bases, as shown in

[1] Ph. Lenard and V. Klatt. Ann. d. Phys., 15, p. 225–282, 633–672 (1904).

showed, besides the four normal sets of manganese, four sets differing from the normal ones by $\Delta(1/\lambda) = 5.4$. (See section II for an account of such anomalous sets.)

[3] A mixture of 70 per cent BaS and 30 per cent SrS, with Li_3PO_4 as the flux (L. and K. No. 35), gave a spectrum curve such as would be obtained by superposing the separate curves given by BaS and SrS. A mixture of equal parts of BaS, SrS, and CaS with Li_3PO_4 and Li_2SO_4 as the fluxes (L. and K. No. 41) gave a curve such as would be obtained by superposing the curves of CaS and SrS, the maximum due to BaS being scarcely perceptible.

[4] The table here referred to is that giving the sets of bands characteristic of the active metal. (See section IV of this chapter.)

[5] A mixture of SrS and CaS with Na_2SO_4 as the flux (L. and K. No. 34) gave a curve with a broad crest which may possibly represent the superposing of the curves due to SrS and CaS.

[6] All the spectrum curves obtained from solid solutions whose active metal was bismuth were very jagged, so that the resolution into component bands was particularly easily made.

[7] Upon resolving this luminescence into its component bands, two sets with intervals of 17.7 and 18.2 were obtained. These were probably not due to zinc, but to some impurity, since they differ from those found in other solid solutions of zinc, and agree with those found in several samples of zinc sulphides and blendes. (See section VII of this chapter.)

figure 25. Of course it is known that the luminescent color of a solid solution varies according to its previous treatment and the concentration of the active substance,[1] but these causes would not be likely to affect the colors of the Lenard and Klatt sulphides, whose treatment and history are practically the same. Hence we might expect these substances to show some regularity in their properties. In figure 25, points *A* and *B* indicate the probable luminescent color of zinc sulphide with copper and manganese, respectively, as active metal, in case the curves shown in the figure represent a real relation. The colors expected are green and yellow; which expectation is confirmed to some extent by several authors.[2]

SUMMARY OF SECTION III

(1) The cathodo-luminescence spectra of 27 samples of Lenard and Klatt's sulphides were studied spectrophotometrically.

(2) Just as in electrolytes, whatever bases may be used, dissolved active metals show their characteristics. Each active metal shows characteristic sets of constant-frequency interval.

(3) Sets of this kind were determined for copper and manganese. They are the same as those found for these metals in section II.

(4) Sets were likewise determined for lead, bismuth, silver, and antimony. These had not been previously investigated.

(5) In a few cases anomalous sets are found, which can be obtained from the normal sets for the metal in question by the addition of a small constant amount to each member.

(6) The base seems to determine the color of the luminescence.

(7) The flux has no important effect on the color of the luminescence.

(8) Except in the case of zinc, no indication of impurities could be found. If such were present, it was in such a minute percentage as to exert little or no influence on the character of the luminescence.

IV. Solid Solutions of Other Metals

Encouraged by the results obtained so far, the author extended the research to 36 other metals, which brought the total number studied up to 42. The metals were usually obtained in the form of oxides or oxalates, but sometimes in that of sulphates or of chlorides. The bases usually employed were calcium carbonate containing traces of manganese and calcium fluoride containing traces of manganese and samarium. Both of these were made by Kahlbaum.

[1] E. Becquerel. Ann. chim. et phys., 3, 55, p. 5–119 (1859). A Verneuil. C. R. (103), p. 600–603 (1886). E. Wiedemann and G. C. Schmidt. Ann. d. Phys. und Chem. 56, p. 201–254 (1895).

[2] H. Grüne. Ber. chem. Ges., 37, 3, 3076-3077 (1904). E. M. Dougall, A. W. Steward, R. Wright. Journ. Chem. Soc. London, 111, p. 663-683 (1917).

In some cases, barium sulphide, strontium sulphide, cadmium sulphate, calcium sulphate, etc., were used, the impurities being carefully determined. The luminescence due to the impurities of the base was by no means negligible, especially when the total luminescence was not very bright, so that it was necessary to remove bands due to these impurities from the newly obtained spectrum curves.

The ratio of the number of atoms of the base to that of those of the active metal was between 100 : 1 and 1,000 : 1, the usual ratio being that which was proved by Bruninghaus[1] to produce the maximum luminescence of calcium salts with manganese as the active substance, namely, 250 : 1. Such solid solutions are rather dilute, but they have this advantage, that the effect of the impurities of the active agent (when of reasonable purity) is necessarily almost imperceptible. Nevertheless, in a few cases bands appeared which had to be attributed to an impurity of the active metal.

The calcination was usually done with a gas-blowpipe, but in some cases in which the luminescence was faint an oxyhydrogen flame was used.

The number (97) of the solid solutions studied is too great to permit a description of the work in detail, but the results (including those described in preceding sections) are given in the following tables:

TABLE VII—*List of preparations and brightness of luminescence*[1, 2]

Activator	Solvent	Fluxes	Brightness	Activator	Solvent	Fluxes	Brightness
(1) Li	$CaCO_3$....	.....	v.d.	(4) Mg	$CaCO_3$.....	.....	m.
	CaF_2.....	.....	v.d.		CaF_2.....	.....	v. d.
(2) Be	$CaCO_3$....	.....	d.	(5) Al	$CaCO_3$.....	.....	v. d.
	CaF_2.....	.....	v. d.		CaF_2.....	.....	d.
	$CaSO_4$....	.....	v. d.		$CaSO_4$.....	.....	v. d.
	$CdSO_4$....	.....	v. d.		$CdSO_4$.....	.....	v. d.
	MgO.....	.....	v. d.	(6) K	$CaCO_3$.....	.....	d.
	ZnS.....	.....	d.		CaF_2.....	.....	v. d.
	SrS.....	Na_2SO_4....	v. d.	(7) Ca	BaS.....	Na_2SO_4.....	d.
(3) Na	$CaCO_3$....	.....	v. d.		SrS.....	Na_2SO_4....	m.
	CaF_2.....	.....	v. d.	(8) Ti	$CaCO_3$.....	.....	d.
	$CdSO_4$....	.....	v. d.		CaF_2.....	.....	d.

[1] The intensities of luminescence in this list are approximate and relative; too much stress is not to be laid upon the comparison of the various solid solutions the conditions of excitation of which are inevitably somewhat different.

These intensities are denoted by the following symbols:

(*a*) *v. str*, so strong that the luminescent light had to be greatly reduced for purposes of measurement.

(*b*) *str*, so strong that the light had to be somewhat reduced.

(*c*) *m*, of such intensity that observations could be made with readjustment of light ratios.

(*d*) *d*, so dim that the comparison light had to be somewhat reduced.

(*e*) *v.d*, very dim, so that the comparison light had to be greatly reduced.

[1] M. L. Bruninghaus. C. R., 144, p. 839 (1907).

TABLE VII—*List of preparations and brightness of luminescence*—Continued

Activator	Solvent	Fluxes	Brightness
(9) V	CaF_2		m.
	$CaAl_2O_4$		v. d.
(10) Cr	CaF_2		d.
	SrS	Na_2SO_4	m.
(11) Mn	$CaCO_3$		str.
	$CaSO_4$		str.
	$Ca_3(PO_4)_2$		v. str.
	$ZnSO_4$		m.
	$MgSO_4$		str.
	Alum (NH_4)		d.
	CaS	$Na_2SO_4.CaF_2$	v. str.
	SrS	Na_2SO_4	v. str.
(12) Fe	$CaCO_3$		v. d.
	CaF_2		v. d.
	$CdSO_4$		v. d.
(13) Ni	CaF_2		v. d.
	$CdSO_4$		v. d.
(14) Co	$CaCO_3$		v. d.
	CaF_2		d.
(15) Cu	$CaSO_4$		m.
	$MgSO_4$		d.
	CaS	Li_2SO_4	v. str.
	CaS	$Li_2SO_4.CaF_2$	v. str.
	SrS	CaF_2	v. str.
	SrS	$K_2B_6O_{10}$	v. str.
	SrS	$MgHPO_4$	v. str.
	BaS	NaCl	str.
	BaS	NaF	str.
	BaS	$Na_2B_4O_7$	str.
	CaS ⅓ BaS ⅓ SrS ⅓	Li_3PO_4 Li_2SO_4	v. str.
	SrS ½ BaS ½	Li_3PO_4	v. str.
(16) Zn	$CaCO_3$		m.
	CaF_2		d.
(17) Ga	$CaCO_3$		str.
	CaF_2		m.
(18) Ge	$CaCO_3$		m.
	BaS	Na_2SO_4	m.
	SrS	Na_2SO_4	m.
	CaF_2		m.
(19) Rb	$CaCO_3$		m.
	CaF_2		v. d.
(20) Sr	$CaCO_3$		d.
	CaF_2		m.
(21) Yt	$CaCO_3$		m.
	CaF_2		m.
(22) Zr	$CaCO_3$		m.
	CaF_2		m.
(23) Nb	$CaCO_3$		m.
	CaF_2		m.
(24) Mo	$CaCO_3$		m.
	CaF_2		m.
(25) Ag	SrS	Na_2SO_4	str.
Ag-cont.	SrS	Li_2SO_4 Li_2CO_3	str.
(26) Cd	$CaCO_3$		v. d.
	CaF_2		d.
(27) Sn	$CaCO_3$		m.
	CaF_2		str.
	$CdSO_4$		v. d.
(28) Sb	CaS	$Na_2SO_4.NaF$	str.
(29) Ba	$CaCO_3$		m.
	CaF_2		d.
(30) La	CaF_2		d.
	$CdSO_4$		v. d.
(31) Ce	$CaCO_3$		d.
	CaF_2		m.
(32) Pr	$CaCO_3$		str.
	CaF_2		m.
	BaS	Na_2SO_4	m.
	SrS	Na_2SO_4	str.
(33) Nd	$CaCO_3$		m.
	CaF_2		m.
	ZnS		m.
	BaS	Na_2SO_4	d.
	SrS	Na_2SO_4	d.
(34) Sa	$CaCO_3$		str.
	CaF_2		str.
	BaS	Na_2SO_4	m.
	SrS	Na_2SO_4	str.
(35) Gd	$CaCO_3$		m.
	CaF_2		m.
	BaS	Na_2SO_4	d.
	SrS	Na_2SO_4	d.
(36) Dy	$CaCO_3$		str.
	CaF_2		str.
(37) Ho	$CaCO_3$		d.
	CaF_2		d.
(38) Er	$CaCO_3$		str.
	CaF_2		str.
	BaS	Na_2SO_4	m.
	SrS	Na_2SO_4	str.
(39) Hg	$CaCO_3$		v. d.
	CaF_2		v. d.
	$CdSO_4$		v. d.
(40) Tl	CaF_2		m.
	BaS	Na_2SO_4	m.
	SrS	Na_2SO_4	m.
(41) Pb	CaS	$Na_2SO_4.NaF$	v. str.
	SrS	NaF	str.
	SrS	$Na_2SO_4.NaF$	v. str.
	BaS	Na_2SO_4	m.
(42) Bi	CaS	[3]	v. str.
	SrS	Na_2SO_4	str.
	BaS	$Na_2B_4O_7$	v. str.
	BaS	$K_2B_6O_{10}$	v. str.
	CaS SrS	Na_2SO_4	v. str.

[3] Fluxes with Bi CaS were: Li_2SO_4, Na_2SO_4, CaF_2, $Na_2B_4O_7$.

V. NUMERICAL RESULTS

TABLE VIII[1]—*Constant-frequency interval sets*

[Throughout these tables, λ is measured in Å. U., and 1/λ in 1/Å. U. × 10^7. In each table, each separate series is given in a separate column.]

PART 1—*Lithium.* Intervals, 121.8, 123.6

Set I		Set II	
λ	1/λ	λ	1/λ
5,168	1,935.0	5,250	1,904.8
4,862	2,056.8	4,930	2,028.4
4,590	2,178.6	4,647	2,152.0

PART 2—*Glucinum.* Interval, 114.5

Set I		Set II	
λ	1/λ	λ	1/λ
5,764	1,734.8	5,580	1,792.1
5,407	1,849.3	5,245	1,906.6
5,092	1,963.8	4,948	2,021.1
4,812	2,078.3	4,682	2,135.6
4,560	2,192.8		

PART 3—*Sodium.* Interval, 70.0

Set I		Set II	
λ	1/λ	λ	1/λ
5,600	1,785.7	5,492	1,820.7
5,389	1,855.7	5,289	1,890.7
5,193	1,925.7	5,100	1,960.7
5,011	1,995.7	4,924	2,030.7
4,841	2,065.7	4,760	2,100.7

PART 4—*Magnesium.* Interval, 65.7

6,143	1,627.8	5,112	1,956.3
5,905	1,693.5	4,946	2,022.0
5,684	1,759.2	4,790	2,087.7
5,480	1,824.9	4,644	2,153.4
5,289	1,890.6	4,506	2,219.1

PART 5—*Aluminum.* Interval, 59.8

5,843	1,711.3	5,127	1,950.5
5,646	1,771.1	4,974	2,010.3
5,462	1,830.9	4,831	2,070.1
5,289	1,890.7	4,695	2,129.9

PART 6—*Potassium.* Interval, sets I-II, 46.5; sets III-IV, 51.2

Set I		Set III	
λ	1/λ	λ	1/λ
6,010	1,663.9	6,085	1,643.4
5,846	1,710.4	5,901	1,694.6
5,692	1,756.9	5,728	1,745.8
5,545	1,803.4	5,565	1,797.0
5,405	1,849.9	5,411	1,848.2
5,273	1,896.4	5,265	1,899.4
5,147	1,942.9	5,127	1,950.6
5,027	1,989.4	4,996	2,001.8
4,912	2,035.9	4,871	2,053.0
4,802	2,082.4	4,752	2,104.2
4,697	2,128.9		

Set II		Set IV	
λ	1/λ	λ	1/λ
5,960	1,678.0	6,008	1,664.4
5,799	1,724.5	5,829	1,715.6
5,647	1,771.0	5,660	1,766.8
5,502	1,817.5	5,501	1,818.0
5,365	1,864.0	5,350	1,869.2
5,234	1,910.5	5,207	1,920.4
5,110	1,957.0	5,072	1,971.6
4,991	2,003.5	4,944	2,022.8
4,878	2,050.0	4,822	2,074.0
4,770	2,096.5	4,705	2,125.2

PART 7—*Calcium.* Interval, sets I-II, 42.6; sets III-IV, 48.7

Set I		Set III	
λ	1/λ	λ	1/λ
5,724	1,747.0	5,810	1,721.2
5,588	1,789.6	5,650	1,769.9
5,458	1,832.2	5,499	1,818.6
5,334	1,874.8	5,355	1,867.3
5,215	1,917.4	5,219	1,916.0
5,102	1,960.0	5,090	1,964.7

Set II		Set IV	
λ	1/λ	λ	1/λ
5,778	1,730.7	5,862	1,705.8
5,639	1,773.3	5,700	1,754.5
5,507	1,815.9	5,546	1,803.2
5,381	1,858.5	5,400	1,851.9
5,260	1,901.1	5,261	1,900.6
5,145	1,943.7	5,130	1,949.3
5,034	1,986.3	5,005	1,998.0

[1] The characteristic sets for each active metal, as found from the spectrophotometric observations of the luminescence, are given in the 42 parts of this table. Since these were the *chief determinations* of the investigation, each set was deduced from at least 10 and sometimes as many as 70 experiments, where each experiment consisted of at least 20 and sometimes as many as 60 readings.

TABLE VIII—*Constant-frequency interval sets*—Continued

PART 8—*Titanium*. Interval, 42.4

Set I		Set II	
λ	1/λ	λ	1/λ
5,286	1,891.8	5,227	1,913.0
5,170	1,934.2	5,114	1,955.4
5,059	1,976.6	5,006	1,997.8
4,953	2,019.0	4,901	2,040.2
4,851	2,061.4	4,802	2,082.6
4,753	2,103.8	4,706	2,125.0
4,659	2,146.2	4,614	2,167.4
4,569	2,188.6	4,525	2,209.8

PART 9—*Vanadium*. Interval, sets I-II, 39.2; sets III-IV, 40.5

Set I		Set III	
5,334	1,874.7	5,312	1,882.6
5,225	1,913.9	5,200	1,923.1
5,120	1,953.1	5,093	1,963.6
5,019	1,992.3	4,990	2,004.1
4,922	2,031.5	4,891	2,044.6
4,829	2,070.7	4,796	2,085.1
4,740	2,109.9	4,705	2,125.6
4,653	2,149.1	4,617	2,166.1
Set II		**Set IV**	
5,226	1,898.8	5,295	1,888.6
5,160	1,938.0	5,184	1,929.1
5,058	1,977.2	4,975	2,010.1
4,959	2,016.4	4,877	2,050.6
4,865	2,055.6	4,782	2,091.1
4,774	2,094.8	4,691	2,131.6
4,686	2,134.0	4,604	2,172.1

PART 10—*Chromium*. Interval, sets I-II, 36.4; sets III-IV, 42.3

Set I		Set II	
6,306	1,585.7	6,235	1,603.9
6,165	1,622.1	6,096	1,640.3
6,030	1,658.5	5,964	1,676.7
5,900	1,694.9	5,837	1,713.1
5,776	1,731.3	5,716	1,749.5
5,657	1,767.7	5,599	1,785.9
5,543	1,804.1	5,488	1,822.3
5,433	1,840.5	5,380	1,858.7
5,328	1,876.9	5,277	1,895.1
5,227	1,913.3	5,177	1,931.5
5,129	1,949.7	5,082	1,967.9
5,035	1,986.1	4,989	2,004.3
4,944	2,022.5	4,900	2,040.7
4,857	2,058.9	4,814	2,077.1

PART 10—*Chromium*—Continued

Set III		Set IV	
λ	1/λ	λ	1/λ
6,342	1,576.8	6,256	1,598.5
6,176	1,619.1	6,095	1,640.8
6,019	1,661.4	5,941	1,683.1
5,870	1,703.7	5,796	1,725.4
5,726	1,746.0	5,657	1,767.7
5,592	1,788.3	5,525	1,810.0
5,463	1,830.6	5,399	1,852.3
5,339	1,872.9	5,278	1,894.6
5,221	1,915.2	5,163	1,936.9
5,108	1,957.5	5,052	1,979.2
5,000	1,999.8	4,947	2,021.5
4,897	2,042.1	4,845	2,063.8
4,798	2,084.4	4,748	2,106.1
4,702	2,126.7		

PART 11—*Manganese*. Interval, sets I-II, 34; sets III-IV, 42

Set I		Set II	
6,649	1,504	5,574	1,794
6,502	1,538	5,470	1,828
6,361	1,572	5,371	1,862
6,227	1,606	5,274	1,896
6,098	1,640	5,181	1,930
5,974	1,674	5,092	1,964
5,855	1,708	5,005	1,998
5,741	1,742	4,921	2,032
5,631	1,776	4,840	2,066
5,525	1,810	4,762	2,100
5,423	1,844	4,686	2,134
5,325	1,878	4,613	2,168
5,220	1,912	4,541	2,202
5,139	1,946		
5,051	1,980		
4,965	2,014		
4,883	2,048		
4,803	2,082		
4,726	2,116		
4,651	2,150		
4,579	2,184		
4,509	2,218		
Set II		**Set III**	
6,570	1,522	6,645	1,505
6,427	1,556	6,464	1,547
6,289	1,590	6,293	1,589
6,158	1,624	6,131	1,631
6,031	1,658	5,977	1,673
5,910	1,692	5,831	1,715
5,794	1,726	5,691	1,757
5,682	1,760	5,559	1,799
		5,432	1,841
		5,311	1,883
		5,195	1,925
		5,084	1,967
		4,978	2,009
		4,874	2,051
		4,778	2,093
		4,684	2,135
		4,593	2,177
		4,507	2,219

TABLE VIII—*Constant-frequency interval sets*—Continued

PART 11—*Manganese*—Continued

λ	1/λ	λ	1/λ
Set IV		Set IV	
6,544	1,528	5,247	1,906
6,369	1,570	5,133	1,948
6,203	1,612	5,025	1,990
6,046	1,654	4,921	2,032
5,896	1,696	4,822	2,074
5,754	1,738	4,726	2,116
5,618	1,780	4,634	2,158
5,488	1,822	4,545	2,200
5,365	1,864		

PART 12—*Iron*. Interval, 37.4

Set I		Set II	
6,070	1,647.5	6,002	1,666.2
5,935	1,684.9	5,870	1,703.6
5,806	1,722.3	5,744	1,741.0
5,683	1,759.7	5,623	1,778.4
5,564	1,797.1	5,507	1,815.8
5,451	1,834.5	5,396	1,853.2
5,342	1,871.9	5,289	1,890.6
5,238	1,909.3	5,187	1,928.0
5,137	1,946.7	5,088	1,965.4
5,040	1,984.1	4,993	2,002.8
4,947	2,021.5	4,901	2,040.2
4,857	2,058.9	4,813	2,077.6
4,770	2,096.3	4,728	2,115.0
4,687	2,133.7	4,646	2,152.4
4,606	2,171.1	4,567	2,189.8
4,528	2,208.5	4,490	2,227.2

PART 13—*Nickel*. Interval, set I, 36.0; set II, 36.7

Set I		Set II	
5,216	1,917.1	5,268	1,898.2
5,120	1,953.1	5,168	1,934.9
5,027	1,989.1	5,072	1,971.6
4,938	2,025.1	4,979	2,008.3
4,852	2,061.1	4,890	2,045.0
4,768	2,097.1	4,804	2,081.7

PART 14—*Cobalt*—Interval, sets I-II, 32.2; set III, 39.9

Set I		Set I	
5,278	1,894.7	4,864	2,055.7
5,190	1,926.9	4,789	2,087.9
5,104	1,959.1	4,717	2,120.1
5,022	1,991.3	4,646	2,152.3
4,942	2,023.5		

PART 14—*Cobalt*—Continued

Set II		Set III	
5,233	1,910.8	5,268	1,898.1
5,147	1,943.0	5,160	1,938.0
5,063	1,975.2	5,056	1,977.9
4,982	2,007.4	4,956	2,017.8
4,903	2,039.6	4,860	2,057.7
4,827	2,071.8	4,767	2,097.6
4,753	2,104.0	4,678	2,137.5
4,681	2,136.2		
4,612	2,168.4		

PART 15—*Copper*. Interval, 34

Set I		Set II	
6,309	1,585	6,242	1,602
6,177	1,619	6,112	1,636
6,050	1,653	5,988	1,670
5,928	1,687	5,869	1,704
5,811	1,721	5,754	1,738
5,698	1,755	5,643	1,772
5,590	1,789	5,537	1,806
5,485	1,823	5,435	1,840
5,385	1,857	5,336	1,874
5,288	1,891	5,241	1,908
5,195	1,925	5,149	1,942
5,105	1,959	5,060	1,976
5,018	1,993	4,975	2,010
4,933	2,027	4,892	2,044
4,852	2,061	4,812	2,078
4,773	2,095	4,735	2,112
4,697	2,129	4,660	2,146
4,623	2,163	4,587	2,180
4,552	2,197	4,517	2,214
4,482	2,231		

PART 16—*Zinc*. Interval, 32.6

Set I		Set II	
5,385	1,857.0	5,440	1,838.3
5,292	1,889.6	5,345	1,870.9
5,202	1,922.2	5,254	1,903.5
5,115	1,954.8	5,165	1,936.1
5,032	1,987.4	5,079	1,968.7
4,950	2,020.0	4,997	2,001.3
4,872	2,052.6	4,917	2,033.9
4,796	2,085.2	4,839	2,066.5
4,722	2,117.8	4,764	2,099.1
4,650	2,150.4	4,691	2,131.7
4,581	2,183.0	4,620	2,164.3
4,513	2,215.6	4,552	2,196.9

TABLE VIII—*Constant-frequency interval sets*—Continued

PART 17—*Gallium*. Interval, 30.2

Set I		Set II	
λ	1/λ	λ	1/λ
5,466	1,829.4	5,016	1,993.5
5,377	1,859.6	4,941	2,023.7
5,292	1,889.8	4,869	2,053.9
5,208	1,920.0	4,798	2,084.1
5,128	1,950.2	4,730	2,114.3
5,049	1,980.4		
4,974	2,010.6		
4,900	2,040.8		
4,829	2,071.0		
4,759	2,101.2		

Set II		Set III	
λ	1/λ	λ	1/λ
5,427	1,842.5	5,407	1,849.3
5,340	1,872.7	5,321	1,879.5
5,255	1,902.9	5,236	1,909.7
5,173	1,933.1	5,155	1,939.9
5,093	1,963.3	5,076	1,970.1
		4,999	2,000.3
		4,925	2,030.5
		4,853	2,060.7
		4,783	2,090.9
		4,714	2,121.1

PART 18—*Germanium*. Interval, 28.4

Set I		Set II	
λ	1/λ	λ	1/λ
6,399	1,562.7	6,341	1,576.9
6,285	1,591.1	6,229	1,605.3
6,175	1,619.5	6,121	1,633.7
6,068	1,647.9	6,016	1,662.1
5,966	1,676.3	5,915	1,690.5
5,866	1,704.7	5,818	1,718.9
5,770	1,733.1	5,723	1,747.3
5,677	1,761.5	5,631	1,775.7
5,587	1,789.9	5,543	1,804.1
5,500	1,818.3	5,457	1,832.5
5,415	1,846.7	5,374	1,860.9
5,333	1,875.1	5,293	1,889.3

PART 19—*Rubidium*. Interval, 25.6

Set I		Set I	
λ	1/λ	λ	1/λ
5,514	1,813.6	4,715	2,120.8
5,437	1,839.2	4,659	2,146.4
5,363	1,864.8	4,604	2,172.0
5,290	1,890.4	4,550	2,197.6
5,219	1,916.0	4,498	2,223.2
5,150	1,941.6		
5,083	1,967.2		
5,018	1,992.0		
4,954	2,018.4		
4,892	2,044.0		
4,832	2,069.6		
4,773	2,095.2		

PART 19—*Rubidium*—Continued

Set II		Set III	
λ	1/λ	λ	1/λ
5,255	1,903.2		
5,185	1,928.8	4,792	2,086.6
5,117	1,954.4	4,734	2,112.2
5,051	1,980.0	4,678	2,137.8
4,986	2,005.6	4,622	2,163.4
4,923	2,031.2	4,568	2,189.0
4,862	2,056.8	4,515	2,214.6
4,802	2,082.4		
4,744	2,108.0		
4,687	2,133.6		
4,631	2,159.2		
4,577	2,184.8		
4,524	2,210.4		

Set III		Set IV	
λ	1/λ	λ	1/λ
5,540	1,805.0	5,501	1,817.8
5,463	1,830.6	5,425	1,843.4
5,387	1,856.2	5,351	1,869.0
5,314	1,881.8	5,278	1,894.6
5,243	1,907.4	5,208	1,920.2
5,173	1,933.0	5,139	1,945.8
5,106	1,958.6	5,072	1,971.4
5,040	1,984.2	5,008	1,997.0
4,976	2,009.8	4,944	2,022.6
4,913	2,035.4	4,882	2,048.2
4,852	2,061.0	4,822	2,073.8
		4,763	2,099.4
		4,706	2,125.0
		4,650	2,150.6
		4,595	2,176.2
		4,542	2,201.8
		4,489	2,227.4

PART 20—*Strontium*. Interval, sets I-II, 22.5; sets III-IV, 27.5

Set I		Set I	
λ	1/λ	λ	1/λ
6,112	1,636.2	4,692	2,131.2
6,029	1,658.7	4,643	2,153.7
5,948	1,681.2	4,595	2,176.2
5,870	1,703.7	4,548	2,198.7
5,793	1,726.2	4,502	2,221.2
5,719	1,748.7		
5,646	1,771.2		
5,575	1,793.7		
5,506	1,816.2		
5,439	1,838.7		
5,373	1,861.2		
5,309	1,883.7		
5,246	1,906.2		
5,185	1,928.7		
5,125	1,951.2		
5,067	1,973.7		
5,010	1,996.2		
4,954	2,018.7		
4,899	2,041.2		
4,846	2,063.7		
4,794	2,086.2		
4,742	2,108.7		

Set II	
λ	1/λ
6,070	1,647.4
5,988	1,669.9
5,909	1,692.4
5,831	1,714.9
5,756	1,737.4
5,682	1,759.9
5,610	1,782.4
5,540	1,804.9
5,472	1,827.4
5,406	1,849.9
5,341	1,872.4
5,277	1,894.9
5,215	1,917.4

TABLE VIII—*Constant-frequency interval sets*—Continued

PART 20—*Strontium*—Continued

λ	1/λ
Set II—continued	
5,155	1,939.9
5,096	1,962.4
5,038	1,984.9
4,982	2,007.4
4,926	2,029.9
4,872	2,052.4
4,820	2,074.9
4,768	2,097.4
4,717	2,119.9
4,668	2,142.4
4,619	2,164.9
4,572	2,187.4
4,525	2,209.9
Set III	
6,109	1,636.9
6,008	1,664.4
5,911	1,691.9
5,816	1,719.4
5,725	1,746.9
5,636	1,774.4
5,550	1,801.9
5,466	1,829.4
5,385	1,856.9
5,307	1,884.4
5,231	1,911.9
5,156	1,939.4
5,084	1,966.9
5,014	1,994.4
4,946	2,021.9
Set III	
4,880	2,049.4
4,815	2,076.9
4,752	2,104.4
4,691	2,131.9
4,631	2,159.4
4,573	2,186.9
4,516	2,214.4
Set IV	
6,058	1,650.6
5,959	1,678.1
5,863	1,705.6
5,770	1,733.1
5,680	1,760.6
5,593	1,788.1
5,508	1,815.6
5,426	1,843.1
5,346	1,870.6
5,268	1,898.1
5,193	1,925.6
5,120	1,953.1
5,049	1,980.6
4,980	2,008.1
4,913	2,035.6
4,847	2,063.1
4,783	2,090.6
4,721	2,118.1
4,661	2,145.6
4,602	2,173.1
4,544	2,200.6

PART 21—*Yttrium*. Intervals, 22.3, 24.3

Set I		Set I	
6,308	1,585.3	5,033	1,986.7
6,220	1,607.6	4,978	2,009.0
6,135	1,629.9	4,923	2,031.3
6,053	1,652.2	4,869	2,053.6
5,972	1,674.5	4,817	2,075.9
5,893	1,696.8	4,766	2,098.2
5,817	1,719.1	4,716	2,120.5
5,742	1,741.4	4,667	2,142.8
5,670	1,763.7	4,619	2,165.1
5,599	1,786.0	4,572	2,187.4
5,530	1,808.3	4,525	2,209.7
5,463	1,830.6		
5,397	1,852.9	Set II	
5,333	1,875.2		
5,270	1,897.5		
5,209	1,919.8	6,292	1,589.3
5,149	1,942.1	6,197	1,613.6
5,091	1,964.4	6,105	1,637.9

PART 21—*Yttrium*—Continued

Set II		Set II	
6,016	1,662.2	5,118	1,953.8
5,929	1,686.5	5,055	1,978.1
5,845	1,710.8	4,994	2,002.4
5,763	1,735.1	4,934	2,026.7
5,684	1,759.4	4,876	2,051.0
5,606	1,783.7	4,819	2,075.3
5,531	1,808.0	4,763	2,099.6
5,458	1,832.3	4,708	2,123.9
5,386	1,856.6	4,655	2,148.2
5,317	1,880.9	4,603	2,172.5
5,249	1,905.2	4,552	2,196.8
5,183	1,929.5	4,502	2,221.1

PART 22—*Zirconium*. Intervals, 22.7, 24.2

Set I		Set II	
5,342	1,872.0	5,387	1,856.3
5,278	1,894.7	5,318	1,880.5
5,215	1,917.4	5,250	1,904.7
5,154	1,940.1	5,184	1,928.9
5,095	1,962.8	5,120	1,953.1
5,037	1,985.5	5,057	1,977.3
4,980	2,008.2	4,996	2,001.5
4,924	2,030.9	4,937	2,025.7
4,869	2,053.6	4,878	2,049.9
4,816	2,076.3	4,821	2,074.1
4,764	2,099.0	4,766	2,098.3
4,713	2,121.7	4,711	2,122.5
4,663	2,144.4	4,658	2,146.7
4,614	2,167.1	4,606	2,170.9
4,567	2,189.8	4,556	2,195.1
		4,506	2,219.3

PART 23—*Columbium* (*Niobium*). Intervals, 21.5, 25.5

Set I		Set II	
5,411	1,848.2	5,429	1,841.9
5,348	1,869.7	5,355	1,867.4
5,288	1,891.2	5,283	1,892.9
5,228	1,912.7	5,213	1,918.4
5,170	1,934.2	5,144	1,943.9
5,113	1,955.7	5,078	1,969.4
5,058	1,977.2	5,013	1,994.9
5,003	1,998.7	4,950	2,020.4
4,950	2,020.2	4,888	2,045.9
4,898	2,041.7	4,828	2,071.4
4,847	2,063.2	4,769	2,096.9
4,797	2,084.7	4,712	2,122.4
4,748	2,106.2	4,656	2,147.9
4,700	2,127.7	4,601	2,173.4
4,653	2,149.2	4,548	2,198.9
4,607	2,170.7		
4,562	2,192.2		

TABLE VIII—*Constant-frequency interval sets*—Continued

PART 24—*Molybdenum.* Interval, sets I-II 20.9; sets III-IV, 23.6

λ	1/λ	λ	1/λ
Set I		Set III	
5,484	1,823.3	5,485	1,823.1
5,422	1,844.2	5,415	1,846.7
5,362	1,865.1	5,347	1,870.3
5,302	1,886.0	5,280	1,893.9
5,244	1,906.9	5,215	1,917.5
5,187	1,927.8	5,152	1,941.1
5,132	1,948.7	5,090	1,964.7
5,077	1,969.6	5,029	1,988.3
5,024	1,990.5	4,970	2,011.9
4,972	2,011.4	4,913	2,035.5
4,921	2,032.3	4,856	2,059.1
4,870	2,053.2	4,801	2,082.7
4,821	2,074.1	4,748	2,106.3
4,773	2,095.0	4,695	2,129.9
4,726	2,115.9	4,644	2,153.5
4,680	2,136.8		
4,635	2,157.7		
Set II		Set IV	
5,453	1,833.7	5,450	1,834.9
5,392	1,854.6	5,381	1,858.5
5,332	1,875.5	5,313	1,882.1
5,273	1,896.4	5,247	1,905.7
5,216	1,917.3	5,183	1,929.3
5,159	1,938.2	5,121	1,952.9
5,104	1,959.1	5,059	1,976.5
5,050	1,980.0	5,000	2,000.1
4,998	2,000.9	4,941	2,023.7
4,946	2,021.8	4,884	2,047.3
4,895	2,042.7	4,829	2,070.9
4,846	2,063.6	4,774	2,094.5
4,797	2,084.5	4,721	2,118.1
4,750	2,105.4	4,669	2,141.7
4,703	2,126.3	4,618	2,165.3
4,657	2,147.2		
4,612	2,168.1		

PART 25—*Silver.* Interval, 21.2

Set I		Set I	
5,873	1,702.6	5,055	1,978.2
5,801	1,723.8	5,001	1,999.4
5,731	1,745.0	4,949	2,020.6
5,662	1,766.2	4,898	2,041.8
5,595	1,787.4	4,847	2,063.0
5,529	1,808.6	4,798	2,084.2
5,465	1,829.8	4,750	2,105.4
5,402	1,851.0	4,702	2,126.6
5,341	1,872.2	4,656	2,147.8
5,281	1,893.4	4,610	2,169.0
5,223	1,914.6	4,566	2,190.2
5,166	1,935.8	4,522	2,211.4
5,110	1,957.0		

PART 25—*Silver*—Continued

λ	1/λ	λ	1/λ
Set II		Set II	
5,914	1,690.9	5,085	1,966.5
5,841	1,712.1	5,031	1,987.7
5,769	1,733.3	4,978	2,008.9
5,700	1,754.5	4,926	2,030.1
5,632	1,775.7	4,875	2,051.3
5,565	1,796.9	4,825	2,072.5
5,500	1,818.1	4,776	2,093.7
5,437	1,839.3	4,728	2,114.9
5,375	1,860.5	4,681	2,136.1
5,314	1,881.7	4,635	2,157.3
5,255	1,902.9	4,590	2,178.5
5,197	1,924.1	4,546	2,199.7
5,141	1,945.3		

PART 26—*Cadmium.* Intervals, 18.7, 22.6

Set I		Set II	
5,686	1,758.6	5,685	1,759.1
5,640	1,777.3	5,613	1,781.7
5,568	1,796.0	5,542	1,804.3
5,511	1,814.7	5,474	1,826.9
5,454	1,833.4	5,407	1,849.5
5,399	1,852.1	5,342	1,872.1
5,345	1,870.8	5,278	1,894.7
5,292	1,889.5	5,216	1,917.3
5,241	1,908.2	5,155	1,939.9
5,190	1,926.9	5,096	1,962.5
5,140	1,945.6	5,038	1,985.1
5,091	1,964.3	4,981	2,007.7
5,043	1,983.0	4,925	2,030.3
4,996	2,001.7	4,871	2,052.9
4,950	2,020.4	4,818	2,075.5
4,904	2,039.1		
4,857	2,058.8		
4,816	2,076.5		

PART 27—*Tin.* Intervals, 19.9, 20.6

Set I		Set I	
5,863	1,705.5	5,197	1,924.4
5,796	1,725.4	5,143	1,944.3
5,730	1,745.3	5,091	1,964.2
5,665	1,765.2	5,040	1,984.1
5,602	1,785.1	4,990	2,004.0
5,540	1,805.0	4,941	2,023.9
5,480	1,824.9	4,893	2,043.8
5,421	1,844.8	4,846	2,063.7
5,363	1,864.7	4,799	2,083.6
5,306	1,884.6	4,754	2,103.5
5,251	1,904.5	4,709	2,123.4

TABLE VIII—*Constant-frequency interval sets*—Continued

PART 27—*Tin*—Continued

Set I—continued		Set II	
λ	1/λ	λ	1/λ
4,666	2,143.3	5,287	1,891.6
4,623	2,163.2	5,230	1,912.2
4,581	2,183.1	5,174	1,932.8
		5,119	1,953.4
Set II		5,066	1,974.0
		5,014	1,994.6
		4,962	2,015.2
5,861	1,706.1	4,912	2,035.8
5,791	1,726.8	4,863	2,056.4
5,723	1,747.4	4,815	2,077.0
5,656	1,768.0	4,767	2,097.6
5,591	1,788.6	4,721	2,118.2
5,527	1,809.2	4,675	2,138.8
5,465	1,829.8	4,631	2,159.4
5,404	1,850.4	4,587	2,180.0
5,345	1,871.0		

PART 28—*Antimony*. Intervals, 19.1, 21.2

Set I		Set II	
5,456	1,832.8	5,267	1,898.7
5,400	1,851.9	5,209	1,919.9
5,345	1,871.0	5,152	1,941.1
5,291	1,890.1	5,096	1,962.3
5,238	1,909.2	5,042	1,983.5
5,186	1,928.3	4,988	2,004.7
5,135	1,947.4	4,936	2,025.9
5,085	1,966.5	4,885	2,047.1
		4,835	2,068.3
Set II		4,786	2,089.5
		4,738	2,110.7
		4,691	2,131.9
5,387	1,856.3		
5,326	1,877.5		

PART 29—*Barium*. Intervals, 19.9, 20.3

Set I		Set I	
6,319	1,582.6	5,490	1,821.4
6,240	1,602.5	5,431	1,841.3
6,164	1,622.4	5,373	1,861.2
6,089	1,642.3	5,316	1,881.1
6,016	1,662.2	5,260	1,901.0
5,945	1,682.1	5,206	1,920.9
5,875	1,702.0	5,152	1,940.8
5,807	1,721.9	5,100	1,960.7
5,741	1,741.8	5,049	1,980.6
5,676	1,761.7	4,999	2,000.5
5,613	1,781.6	4,949	2,020.4
5,551	1,801.5	4,901	2,040.3

PART 29—*Barium*—Continued

Set I—continued		Set II	
λ	1/λ	λ	1/λ
4,854	2,060.2	5,590	1,788.9
4,807	2,080.1	5,527	1,809.2
4,762	2,100.0	5,466	1,829.5
4,717	2,119.9	5,406	1,849.8
4,673	2,139.8	5,347	1,870.1
		5,290	1,890.4
Set II		5,234	1,910.7
		5,179	1,931.0
6,305	1,585.9	5,125	1,951.3
6,226	1,606.2	5,072	1,971.6
6,148	1,626.5	5,020	1,991.9
6,072	1,646.8	4,970	2,012.2
5,999	1,667.1	4,920	2,032.5
5,926	1,687.4	4,871	2,052.8
5,856	1,707.7	4,824	2,073.1
5,787	1,728.0	4,777	2,093.7
5,720	1,748.3	4,731	2,113.7
5,654	1,768.6	4,686	2,134.0

PART 30—*Lanthanum*. Interval, 19.6

Set I		Set II	
5,860	1,706.5	5,829	1,715.6
5,793	1,726.1	5,763	1,735.2
5,728	1,745.7	5,699	1,754.8
5,665	1,765.3	5,636	1,774.4
5,602	1,784.9	5,574	1,794.0
5,542	1,804.5	5,514	1,813.6
5,482	1,824.1	5,455	1,833.2
5,424	1,843.7	5,397	1,852.8
5,367	1,863.3	5,341	1,872.4
5,311	1,882.9	5,285	1,892.0
5,256	1,902.5	5,231	1,911.6
5,203	1,922.1	5,178	1,931.2
5,150	1,941.7	5,126	1,950.8
5,099	1,961.3	5,075	1,970.4
5,048	1,980.9	5,025	1,990.0
4,999	2,000.5	4,976	2,009.6
4,950	2,020.1	4,928	2,029.2
4,903	2,039.7	4,881	2,048.8
4,856	2,059.3	4,835	2,068.4
4,810	2,078.9	4,789	2,088.0
4,765	2,098.5	4,745	2,107.6
4,721	2,118.1	4,701	2,127.2
4,678	2,137.7	4,658	2,146.8
4,636	2,157.3	4,616	2,166.4
4,594	2,176.9	4,575	2,186.0
4,553	2,196.5	4,534	2,205.6

TABLE VIII—*Constant-frequency interval sets*—Continued

PART 31—*Cerium.* Intervals, 17.2, 22.3

λ	1/λ	λ	1/λ
Set I		Set I	
6,270	1,594.8	4,624	2,162.4
6,203	1,612.0	4,588	2,179.6
6,138	1,629.2		
6,074	1,646.4	Set II	
6,011	1,663.6		
5,950	1,680.8		
5,890	1,698.0	6,250	1,600.1
5,830	1,715.2	6,164	1,622.4
5,772	1,732.4	6,080	1,644.7
5,716	1,749.6	5,999	1,667.0
5,660	1,766.8	5,920	1,689.3
5,605	1,784.0	5,842	1,711.6
5,552	1,801.2	5,767	1,733.9
5,499	1,818.4	5,694	1,756.2
5,448	1,835.6	5,623	1,778.5
5,398	1,852.8	5,553	1,800.8
5,348	1,870.0	5,485	1,823.1
5,299	1,887.2	5,419	1,845.4
5,251	1,904.4	5,354	1,867.7
5,204	1,921.6	5,291	1,890.0
5,158	1,938.8	5,229	1,912.3
5,112	1,956.0	5,169	1,934.6
5,068	1,973.2	5,110	1,956.9
5,024	1,990.4	5,053	1,979.2
4,981	2,007.6	4,996	2,001.5
4,939	2,024.8	4,941	2,023.8
4,897	2,042.0	4,887	2,046.1
4,856	2,059.2	4,835	2,068.4
4,816	2,076.4	4,783	2,090.7
4,776	2,093.6	4,733	2,113.0
4,738	2,110.8	4,683	2,135.3
4,699	2,128.0	4,635	2,157.6
4,662	2,145.2	4,587	2,179.9

PART 32—*Præseodymium.* Intervals, 17.0, 21.8

Set I		Set I	
5,892	1,697.2	5,078	1,969.2
5,834	1,714.2	5,035	1,986.2
5,776	1,731.2	4,992	2,003.2
5,720	1,748.2	4,950	2,020.2
5,665	1,765.2	4,909	2,037.2
5,611	1,782.2	4,868	2,054.2
5,558	1,799.2	4,828	2,071.2
5,506	1,816.2	4,789	2,088.2
5,455	1,833.2	4,750	2,105.2
5,405	1,850.2	4,712	2,122.2
5,356	1,867.2	4,675	2,139.2
5,307	1,884.2	4,638	2,156.2
5,260	1,901.2	4,602	2,173.2
5,213	1,918.2	4,566	2,190.2
5,167	1,935.2	4,531	2,207.2
5,122	1,952.2	4,496	2,224.2

PART 32—*Præseodymium*—Continued

λ	1/λ	λ	1/λ
Set II		Set II	
5,880	1,700.7	5,096	1,962.3
5,806	1,722.5	5,040	1,984.1
5,733	1,744.3	4,985	2,005.9
5,662	1,766.1	4,932	2,027.7
5,593	1,787.9	4,879	2,049.5
5,526	1,809.7	4,828	2,071.3
5,460	1,831.5	4,778	2,093.1
5,396	1,853.3	4,728	2,114.9
5,333	1,875.1	4,680	2,136.7
5,272	1,896.9	4,633	2,158.5
5,212	1,918.7	4,587	2,180.3
5,153	1,940.5	4,541	2,202.1

PART 33—*Neodymium.* Intervals, 18.3, 20.1

Set I		Set II	
5,983	1,671.4	5,969	1,675.3
5,918	1,689.7	5,898	1,695.4
5,855	1,708.0	5,829	1,715.5
5,793	1,726.3	5,762	1,735.6
5,732	1,744.6	5,696	1,755.7
5,672	1,762.9	5,631	1,775.8
5,614	1,781.2	5,568	1,795.9
5,557	1,799.5	5,507	1,816.0
5,501	1,817.8	5,446	1,836.1
5,446	1,836.1	5,387	1,856.2
5,393	1,854.4	5,330	1,876.3
5,340	1,872.7	5,273	1,896.4
5,288	1,891.0	5,218	1,916.5
5,238	1,909.3	5,164	1,936.6
5,188	1,927.6	5,111	1,956.7
5,139	1,945.9	5,059	1,976.8
5,091	1,964.2	5,008	1,996.9
5,044	1,982.5	4,958	2,017.0
4,998	2,000.8	4,909	2,037.1
4,953	2,019.1	4,861	2,057.2
4,908	2,037.4	4,814	2,077.3
4,864	2,055.7	4,768	2,097.4
4,822	2,074.0	4,723	2,117.5
4,779	2,092.3	4,678	2,137.6
4,738	2,110.6	4,634	2,157.7
4,697	2,128.9	4,592	2,177.8
4,657	2,147.2	4,550	2,197.9
4,618	2,165.5	4,509	2,218.0
4,579	2,183.8	4,468	2,238.1
4,541	2,202.1		
4,504	2,220.4		
4,467	2,238.7		

TABLE VIII—*Constant-frequency interval sets*—Continued

PART 34—*Samarium.* Intervals, 16.7, 20.8

λ	1/λ	λ	1/λ
Set I		Set I	
6,336	1,578.4	4,553	2,196.4
6,269	1,595.1	4,519	2,213.1
6,204	1,611.8		
6,141	1,628.5	Set II	
6,078	1,645.2		
6,017	1,661.9		
5,957	1,678.6	6,278	1,592.9
5,899	1,695.3	6,197	1,613.7
5,841	1,712.0	6,118	1,634.5
5,785	1,728.7	6,041	1,655.3
5,729	1,745.4	5,966	1,676.1
5,675	1,762.1	5,893	1,696.9
5,622	1,778.8	5,822	1,717.7
5,569	1,795.5	5,752	1,738.5
5,518	1,812.2	5,684	1,759.3
5,468	1,828.9	5,618	1,780.1
5,418	1,845.6	5,553	1,800.9
5,370	1,862.3	5,489	1,821.7
5,322	1,879.0	5,427	1,842.5
5,275	1,895.7	5,367	1,863.3
5,229	1,912.4	5,308	1,884.1
5,183	1,929.2	5,250	1,904.9
5,139	1,945.9	5,193	1,925.7
5,095	1,962.6	5,137	1,946.5
5,052	1,979.3	5,083	1,967.3
5,010	1,996.0	5,030	1,988.1
4,968	2,012.7	4,978	2,008.9
4,928	2,029.4	4,927	2,029.7
4,887	2,046.1	4,877	2,050.5
4,848	2,062.8	4,828	2,071.3
4,809	2,079.5	4,780	2,092.1
4,780	2,096.2	4,733	2,112.9
4,733	2,112.9	4,687	2,133.7
4,696	2,129.6	4,641	2,154.5
4,659	2,146.3	4,597	2,175.3
4,623	2,163.0	4,553	2,196.1
4,588	2,179.7	4,511	2,216.9

PART 35—*Gadolinium.* Interval, 18.6

Set I		Set I	
5,824	1,716.9	5,057	1,977.3
5,762	1,735.5	5,010	1,995.9
5,701	1,754.1	4,964	2,014.5
5,641	1,772.7	4,919	2,033.1
5,583	1,791.3	4,874	2,051.7
5,525	1,809.9	4,830	2,070.3
5,469	1,828.5	4,787	2,088.9
5,414	1,847.1	4,745	2,107.5
5,360	1,865.7	4,704	2,126.1
5,307	1,884.3	4,663	2,144.7
5,255	1,902.9	4,622	2,163.3
5,204	1,921.5	4,583	2,181.9
5,154	1,940.1	4,544	2,200.5
5,105	1,958.7	4,506	2,219.1

PART 35—*Gadolinium*—Continued

λ	1/λ	λ	1/λ
Set II		Set II	
5,797	1,725.1	5,036	1,985.5
5,735	1,743.7	4,990	2,004.1
5,674	1,762.3	4,944	2,022.7
5,615	1,780.9	4,899	2,041.3
5,557	1,799.5	4,854	2,059.9
5,500	1,818.1	4,811	2,078.5
5,444	1,836.7	4,768	2,097.1
5,390	1,855.3	4,727	2,115.7
5,336	1,873.9	4,685	2,134.3
5,284	1,892.5	4,645	2,152.9
5,233	1,911.1	4,605	2,171.5
5,182	1,929.7	4,566	2,190.1
5,133	1,948.3	4,528	2,208.7
5,084	1,966.9		

PART 36—*Dysprosium.* Interval, 18.2

Set I		Set II	
6,312	1,584.4	6,275	1,593.5
6,240	1,602.6	6,205	1,611.7
6,170	1,620.8	6,135	1,629.9
6,101	1,639.0	6,068	1,648.1
6,034	1,657.2	6,001	1,666.3
5,969	1,675.4	5,936	1,684.5
5,905	1,693.6	5,873	1,702.7
5,842	1,711.8	5,811	1,720.9
5,780	1,730.0	5,750	1,739.1
5,720	1,748.2	5,691	1,757.3
5,661	1,766.4	5,632	1,775.5
5,603	1,784.6	5,575	1,793.7
5,547	1,802.8	5,519	1,811.9
5,491	1,821.0	5,464	1,830.1
5,437	1,839.2	5,410	1,848.3
5,384	1,857.4	5,358	1,866.5
5,332	1,875.6	5,306	1,884.7
5,280	1,893.8	5,255	1,902.9
5,230	1,912.0	5,205	1,921.1
5,181	1,930.2	5,157	1,939.3
5,133	1,948.4	5,109	1,957.5
5,085	1,966.6	5,062	1,975.7
5,038	1,984.8	5,015	1,993.9
4,993	2,003.0	4,970	2,012.1
4,947	2,021.2	4,925	2,030.3
4,903	2,039.4	4,882	2,048.5
4,860	2,057.6	4,839	2,066.7
4,817	2,075.8	4,796	2,084.9
4,776	2,094.0	4,755	2,103.1
4,734	2,112.2	4,714	2,121.3
4,694	2,130.4	4,674	2,139.5
4,654	2,148.6	4,634	2,157.7
4,615	2,166.8		

TABLE VIII—*Constant-frequency interval sets*—Continued

PART 37—*Holmium.* Interval, 18.6

λ	1/λ	λ	1/λ
6,011	1,663.5	5,198	1,923.9
5,945	1,682.1	5,148	1,942.5
5,880	1,700.7	5,099	1,961.1
5,816	1,719.3	5,051	1,979.7
5,754	1,737.9	5,004	1,998.3
5,693	1,756.5	4,958	2,016.9
5,633	1,775.1	4,913	2,035.5
5,575	1,793.7	4,868	2,054.1
5,518	1,812.3	4,825	2,072.7
5,462	1,830.9	4,782	2,091.3
5,407	1,849.5	4,740	2,109.9
5,353	1,868.1	4,698	2,128.5
5,300	1,886.7	4,657	2,147.1
5,249	1,905.3	4,617	2,165.7

PART 38—*Erbium.* Interval, 18.3

Set I		Set II	
6,313	1,584.0	6,275	1,593.6
6,241	1,602.3	6,204	1,611.9
6,171	1,620.6	6,134	1,630.2
6,102	1,638.9	6,066	1,648.5
6,034	1,657.2	5,999	1,666.8
5,968	1,675.5	5,934	1,685.1
5,904	1,693.8	5,871	1,703.4
5,841	1,712.1	5,808	1,721.7
5,779	1,730.4	5,747	1,740.0
5,718	1,748.7	5,687	1,758.3
5,659	1,767.0	5,629	1,776.6
5,601	1,785.3	5,571	1,794.9
5,544	1,803.6	5,515	1,813.2
5,489	1,821.9	5,460	1,831.5
5,434	1,840.2	5,406	1,849.8
5,381	1,858.5	5,353	1,868.1
5,328	1,876.8	5,301	1,886.4
5,277	1,895.1	5,250	1,904.7
5,226	1,913.4	5,200	1,923.0
5,177	1,931.7	5,151	1,941.3
5,128	1,950.0	5,103	1,959.6
5,081	1,968.3	5,056	1,977.9
5,034	1,986.6	5,009	1,996.2
4,988	2,004.9	4,964	2,014.5
4,943	2,023.2	4,919	2,032.8
4,898	2,041.5	4,875	2,051.1
4,855	2,059.8	4,832	2,069.4
4,812	2,078.1	4,790	2,087.7
4,770	2,096.4	4,748	2,106.0
4,729	2,114.7	4,707	2,124.3
4,688	2,133.0	4,667	2,142.6
4,648	2,151.3	4,628	2,160.9
4,609	2,169.6	4,589	2,179.2
4,570	2,187.9	4,551	2,197.5
4,533	2,206.2	4,513	2,215.8

PART 39—*Mercury.* Intervals, 17.1, 18.0

λ	1/λ	λ	1/λ
Set I		Set II	
5,822	1,717.5	5,827	1,716.1
5,765	1,734.6	5,767	1,734.1
5,709	1,751.7	5,707	1,752.1
5,654	1,768.8	5,650	1,770.1
5,599	1,785.9	5,593	1,788.1
5,546	1,803.0	5,537	1,806.1
5,494	1,820.1	5,482	1,824.1
5,443	1,837.2	5,429	1,842.1
5,393	1,854.3	5,376	1,860.1
5,343	1,871.4	5,325	1,878.1
5,295	1,888.5	5,274	1,896.1
5,248	1,905.6	5,224	1,914.1
5,201	1,922.7	5,176	1,932.1
5,155	1,939.8	5,128	1,950.1
5,110	1,956.9	5,081	1,968.1
5,066	1,974.0	5,035	1,986.1
5,022	1,991.1	4,990	2,004.1
4,980	2,008.2	4,945	2,022.1
4,938	2,025.3	4,902	2,040.1
4,896	2,042.4	4,859	2,058.1
4,860	2,059.5	4,817	2,076.1
4,816	2,076.6	4,775	2,094.1

PART 40—*Thallium.* Interval, 17.4

6,272	1,594.3	5,242	1,907.5
6,205	1,611.7	5,195	1,924.9
6,138	1,629.1	5,148	1,942.3
6,073	1,646.5	5,103	1,959.7
6,010	1,663.9	5,058	1,977.1
5,948	1,681.3	5,014	1,994.5
5,887	1,698.7	4,970	2,011.9
5,827	1,716.1	4,928	2,029.3
5,769	1,733.5	4,886	2,046.7
5,711	1,750.9	4,845	2,064.1
5,655	1,768.3	4,804	2,081.5
5,600	1,785.7	4,764	2,098.9
5,546	1,803.1	4,725	2,116.3
5,493	1,820.5	4,687	2,133.7
5,441	1,837.9	4,649	2,151.1
5,390	1,855.3	4,611	2,168.5
5,340	1,872.7	4,577	2,184.9
5,291	1,890.1		

PART 41—*Lead.* Intervals, 16.5, 18.5

Set I		Set I	
6,040	1,655.5	5,865	1,705.0
5,981	1,672.0	5,809	1,721.5
5,922	1,688.5	5,754	1,738.0

TABLE VIII—*Constant-frequency interval sets*—Continued

PART 41—*Lead*—Continued				PART 42—*Bismuth*—Continued			
λ	1/λ	λ	1/λ	λ	1/λ	λ	1/λ
Set I—continued		Set II		Set I		Set II	
5,700	1,754.5	6,086	1,643.0	5,716	1,749.5	5,952	1,680.0
5,647	1,771.0	6,019	1,661.5	5,669	1,764.1	5,882	1,700.2
5,594	1,787.5	5,952	1,680.0	5,622	1,778.7	5,813	1,720.4
5,543	1,804.0	5,888	1,698.5	5,576	1,793.3	5,745	1,740.6
5,493	1,820.5	5,824	1,717.0	5,531	1,807.9	5,679	1,760.8
5,444	1,837.0	5,762	1,735.5	5,487	1,822.5	5,615	1,781.0
5,395	1,853.5	5,701	1,754.0	5,443	1,837.1	5,552	1,801.2
5,348	1,870.0	5,642	1,772.5	5,400	1,851.7	5,490	1,821.4
5,301	1,886.5	5,583	1,791.0	5,358	1,866.3	5,430	1,841.6
5,255	1,903.0	5,526	1,809.5	5,317	1,880.9	5,371	1,861.8
5,210	1,919.5	5,470	1,828.0	5,276	1,895.5	5,313	1,882.0
5,165	1,936.0	5,416	1,846.5	5,235	1,910.1	5,257	1,902.2
5,122	1,952.5	5,362	1,865.0	5,196	1,924.7	5,202	1,922.4
5,079	1,969.0	5,309	1,883.5	5,157	1,939.3	5,148	1,942.6
5,037	1,985.5	5,258	1,902.0	5,118	1,953.9	5,095	1,962.8
4,995	2,002.0	5,207	1,920.5	5,080	1,968.5	5,043	1,983.0
4,954	2,018.5	5,157	1,939.0	5,043	1,983.1	4,992	2,003.2
4,914	2,035.0	5,109	1,957.5	5,006	1,997.7	4,942	2,023.4
4,874	2,051.5	5,061	1,976.0	4,969	2,012.3	4,893	2,043.6
4,836	2,068.0	5,014	1,994.5	4,934	2,026.9	4,845	2,063.8
4,797	2,084.5	4,968	2,013.0	4,898	2,041.5	4,798	2,084.0
4,760	2,101.0	4,922	2,031.5	4,864	2,056.1	4,752	2,104.2
4,723	2,117.5	4,878	2,050.0	4,829	2,070.7	4,707	2,124.4
		4,834	2,068.5	4,795	2,085.3	4,663	2,144.6
		4,792	2,087.0	4,762	2,099.9	4,619	2,164.8
		4,749	2,105.5	4,729	2,114.5	4,577	2,185.0
		4,708	2,124.0	4,697	2,129.1	4,535	2,205.2
				4,665	2,143.7	4,494	2,225.4
PART 42—*Bismuth*. Intervals, 14.6, 20.2				4,633	2,158.3	4,453	2,245.6
				4,602	2,172.9	4,413	2,265.8
Set I		Set I		4,571	2,187.5		
				4,541	2,202.1		
5,913	1,691.1	5,813	1,720.3	4,511	2,216.7		
5,863	1,705.7	5,764	1,734.9	4,482	2,231.3		

VI. COMPARISON WITH URBAIN'S RESULTS

An interesting comparison may be made between the above results and those obtained by Urbain,[1] which seem to the present author to be the only dependable measurements hitherto made along this line with the same method of excitation. For the purposes of this comparison, Urbain's results will be considered only for three figures, for the following reasons: (1) his results, being readings of the centers of bands gradually fading on both sides, are essentially approximate only; (2) these bands are often so close together that two or three neighboring bands could easily appear to be but one, and thus introduce rather large errors in Urbain's readings; (3) the fact that each band is a member of a widely extending set gives an elegant check on the reading for each band; were it not so, the

[1] G. Urbain. Ann. chim. et phys. (8), 18, p. 289-386 (1909).

accuracy of the determination would be much reduced; (4) Urbain found the presence of traces of iron, magnesium, manganese, and strontium in the sample of calcium oxide used by him, therefore some of the bands obtained by him are probably due to these impurities, this perhaps accounting for the inconsistency of his results with those obtained by Crookes and by Baur and Marc.

It is not safe to deduce, by extrapolation of the set, the possible positions of bands in a region distant from that observed, since (1) there is no proof that the law of constant intervals holds good outside of the realm of observation (that is, 6,300 to 4,500 Å. U.), and (2) even inside this region, the law may hold only approximately in some parts. Hence the comparison shown in table IX and those found in the next chapter are only trials, to which no real importance is to be attached. The two sets of results show resemblance.

TABLE IX

I. PRÆSODYMIUM

Urbain λ_1 $\mu\mu$	Tanaka λ_2 $\mu\mu$	Two adjacent bands, $\mu\mu$	Dif. $\lambda_2-\lambda_1$ counted up to $\mu\mu$
(1) 678	677.4	684.5, 674.4	−1
(2) 670	669.7	674.4, 664.7	0
(3) 634	633.6	637.0, 628.2	0
(4) 626	626.9	628.2, 620.3	1
(5) 620	619.8	620.3, 613.8	0
(6) 615	613.8	619.8, 611.5	−1
(7) 606.5	607.5	611.5, 603.5	1
(8) 604.5	603.5	607.5, 601.2	−1
(9) 579	579.4, Mn	580.6, 577.6	0
(10) 557	557.4, Mn	559.3, 555.8	0
(11) 552.7	552.6	555.8, 550.6	0
(12) 540.5	540.5	545.5, 539.6	0
(13) 535.5	535.6	539.6, 533.3	0
(14) 525.5	526.0	527.2, 521.2	0.5
(15) 517	516.7	521.2, 515.3	0
(16) 494.0	493.2	495.0, 490.9	−1
(17) 490.5	490.9	493.2, 487.9	0
(18) 487.5	487.9	490.9, 486.8	0

II. NEODYMIUM

Urbain λ_1 $\mu\mu$	Tanaka λ_2 $\mu\mu$	Two adjacent bands, $\mu\mu$	Dif. $\lambda_2-\lambda_1$ counted up to $\mu\mu$
(1) 469	469.7	472.3, 467.8	1
(2) 466	465.7	467.8, 463.4	0
(3) 461	461.8	463.4, 459.2	1
(4) 457.5	457.9	459.2, 455.0	0
(5) 451.5	450.9	454.1, 450.4	−1

TABLE IX—Continued

III. SAMARIUM

Urbain λ_1 $\mu\mu$	Tanaka λ_2 $\mu\mu$	Two adjacent bands, $\mu\mu$	Dif. $\lambda_2-\lambda_1$ ccounted up to $\mu\mu$
(1) 674	672.9, Mn	676.5, 671.7	−1
(2) 666	664.9, Mn	668.9, 662.4	−1
(3) 660.5	661.5	662.4, 654.4	1
(4) 654	654.4	661.5, 653.4	0
(5)*[1] 653	653.4	654.4, 647.2	0
(6) 647	647.2	653.4, 644.6	0
(7) 640.5	640.3	644.6, 636.1	0
(8) 626.5	626.9	627.8, 620.4	0
(9)* 622	622.0, Yt	626.9, 620.4	0
(10) 615.0	614.1	619.7, 611.8	−1
(11) 605.2	604.1	607.8, 601.7	0
(11)* 604.2			
(12) 593.5	593.5, Fe	595.7, 589.9	0
(13) 586.5	585.5, Mn	589.3, 584.1	−1
(14) 579.5	578.5	582.2, 575.2	−1
(15) 576.2	575.2	578.5, 572.9	−1
(16) 572.5	572.9	565.2, 568.4	0
(17)* 571.3	571.1, Tl	572.9, 568.4	0
(18) 568.3	568.4	572.9, 567.5	0
(19)* 567.5	567.5	568.4, 562.2	0
(20) 556.1	556.9	561.8, 555.3	1
(21)* 554	555.3	556.9, 551.8	1
(22) 548.6	548.9	551.8, 546.8	0

Kowalski and Garnier[2]	Tanaka	Kowalski and Garnier[2]	Dif.
(1) 604	604.1	607.8, 601.7	0
(2) 550–560	556.9, 555.3, 551.8	.....	.....

Crookes[3]		Crookes[4]	
(1) 601.5	601.7	604.1, 596.6	0.2
(2) 598.5	599.0, Gd	601.7, 596.6	0.5
(3) 568.9	568.4	572.9, 567.5	−0.5
(4) 551.9	551.8	555.3, 548.9	−0.1
(5) 541.8	541.8	542.7, 537.0	0
(6) 536.5	536.7	537.0, 532.2	0.2
(7) 533.5	533.5, Gd	536.7, 532.2	0

[1] The base used was CaO, except in the case of the numbers marked with an asterisk, in which the base was CaF_2.

[2] M. M. J. de Kowalski and C. Garnier. C.R. 144, p. 836–839 (1907).

[3] W. Crookes. Chem. News, 56, p. 72 (1887).

[4] The coincidence in this case is quite evident. The bands in the first column were picked out from the "alumina-samaria spectra" of Crookes, as newly appeared bands in comparison with the "fractionated alumina spectra" by the same author.

TABLE IX—Continued

IV. DYSPROSIUM[1]

Urbain λ_1 $\mu\mu$	Tanaka λ_2 $\mu\mu$	Two adjacent bands $\mu\mu$	Dif. $\lambda_2-\lambda_1$ counted up to $\mu\mu$
(1)*[2] 684	684.2, Sa	686.6, 682.0	0
(2) 675	673.7	677.8, 669.6	−1
(2)* 673			1
(3) 667	665.6	669.6, 661.5	−1
(4) 662	661.5	665.6, 657.6	−0.5
(5)* 665	655.8, Tl	657.6, 653.6	0
(6) 654.5	653.6	657.6, 649.8	−1
(7)* 599	600.1	603.4, 596.9	1
(8) 595.8	596.9	600.1, 593.6	1
(9)* 590	590.5	593.6, 587.3	0.5
(10) 587.7	587.3	590.5, 584.2	0
(10)* 587.5			
(11) 584.8	584.2	587.3, 581.1	−1
(11)* 584.5			0
(12) 583	583.1, Mn	584.2, 581.1	0
(13) 580.5	581.1	584.2, 578.0	1
(14) 578.5	578.0	581.1, 575.0	−0.5
(15) 577.5	577.0, Sr	578.0, 575.0	−0.5
(16)* 576.5	576.3, Yt	578.0, 575.0	0
(17) 576.3	575.6, Sr	578.0, 575.0	−1
(18) 575.2	575.0	578.0, 572.0	0
(19) 573.5	574.1, Mn	575.0, 572.0	1
(20) 570.8	572.0	575.0, 569.1	1
(21)* 570	569.1	572.0, 566.1	−1
(21) 569			0
(22)* 566	566.1	569.1, 563.2	0
(23) 563.4	563.2	566.1, 560.3	0
(24)* 561.5	561.8, Sa	563.2, 560.3	0
(25)* 550	549.1	551.9, 546.4	−1
(26)* 545.5	545.8, Yt	546.4, 543.7	0
(27)* 540.5	541.0	543.7, 538.4	0.5
(28) 493.5	492.5	594.7, 490.3	−1
(28)* 493.5			
(29) 481.5	481.7	483.9, 479.6	0
(29)* 481.0			1
(30) 479.7	479.6	481.7, 477.6	0
(31) 477	477.6	479.6, 475.5	1
(32)* 475.0	475.5	477.6, 473.4	0.5
(32) 474.8			1
(33) 472.8	473.4	475.5, 471.4	1
(34)* 454.5	453.9	455.8, 452.0	−1
(34) 454			0
(35)* 446.5	446.5	448.3, 444.7	0

[1] The coincidence is not very clear, but perhaps there exists some resemblance.

[2] The base used was CaO, except in the case of the numbers marked with an asterisk, in which the base was CaF_2.

TABLE IX—Continued

V. ERBIUM[1]

Urbain λ_1 $\mu\mu$	Tanaka λ_2 $\mu\mu$	Two adjacent bands $\mu\mu$	Dif. $\lambda_2-\lambda_1$ counted up to $\mu\mu$
(1) 560.3	560.1	562.9, 557.1	0
(2) 533	532.8	535.3, 530.1	0
(3) 528	527.7	530.1, 525.0	0
(4) 478.5	479.0	481.2, 477.0	0
(5) 476	476.2, Mn	477.0, 474.8	0
(6) 473	472.9	474.8, 470.7	0
(7) 469	468.8	470.7, 466.7	0
(8) 467	466.7	468.8, 464.8	0
(9) 462	461.9, Sr	462.8, 460.9	0
(10) 459	458.9	460.9, 457.0	0
(11) 455	455.1	457.0, 453.3	0
(12) 452	451.6, Sr	453.3, 451.3	0

[1]The coincidence is very evident in this case.

VII. RELATION BETWEEN INTERVALS AND ATOMIC WEIGHTS

When some ten active substances had been studied, it was unexpectedly found that a smooth curve could be drawn by plotting the mean value of the characteristic intervals of each active metal as the ordinate against the atomic weight of the metal as the abscissa. This curve was extended to include the whole range of metals studied, and is shown in figure 26.

This is probably a transcendental curve with a somewhat complicated equation. Thus, if the two characteristic intervals of each metal are denoted by d_1 and d_2, and the atomic weight of the same metal by μ, it is probable that the following relations hold:

$$d_1=f(\mu)+\phi(\mu, ,) \qquad d_2=f(\mu)-\phi(\mu, ,)$$

where f is a function of μ only, while ϕ is another function which may contain some other quantities besides μ. Since the difference of the two intervals of one metal is generally small in comparison with the intervals themselves, ϕ must generally be small in comparison with f. The curve in figure 26 corresponds to the equation $y=f(\mu)$.

This relation may be approximate only, and certainly in some cases the deviations are so large that they can scarcely be explained as the result of experimental errors. But this simple relation proved very useful in the present study, as the following instances will show:

(1) In one sample of calcium fluoride (perhaps made by Eimer and Amend) many unknown luminescence bands were found. They constituted two sets, whose mean interval lay on the curve $y=f(\mu)$

in such a position as to indicate that they might be due to samarium. By a subsequent study of several solid solutions of samarium this was proved to be correct.

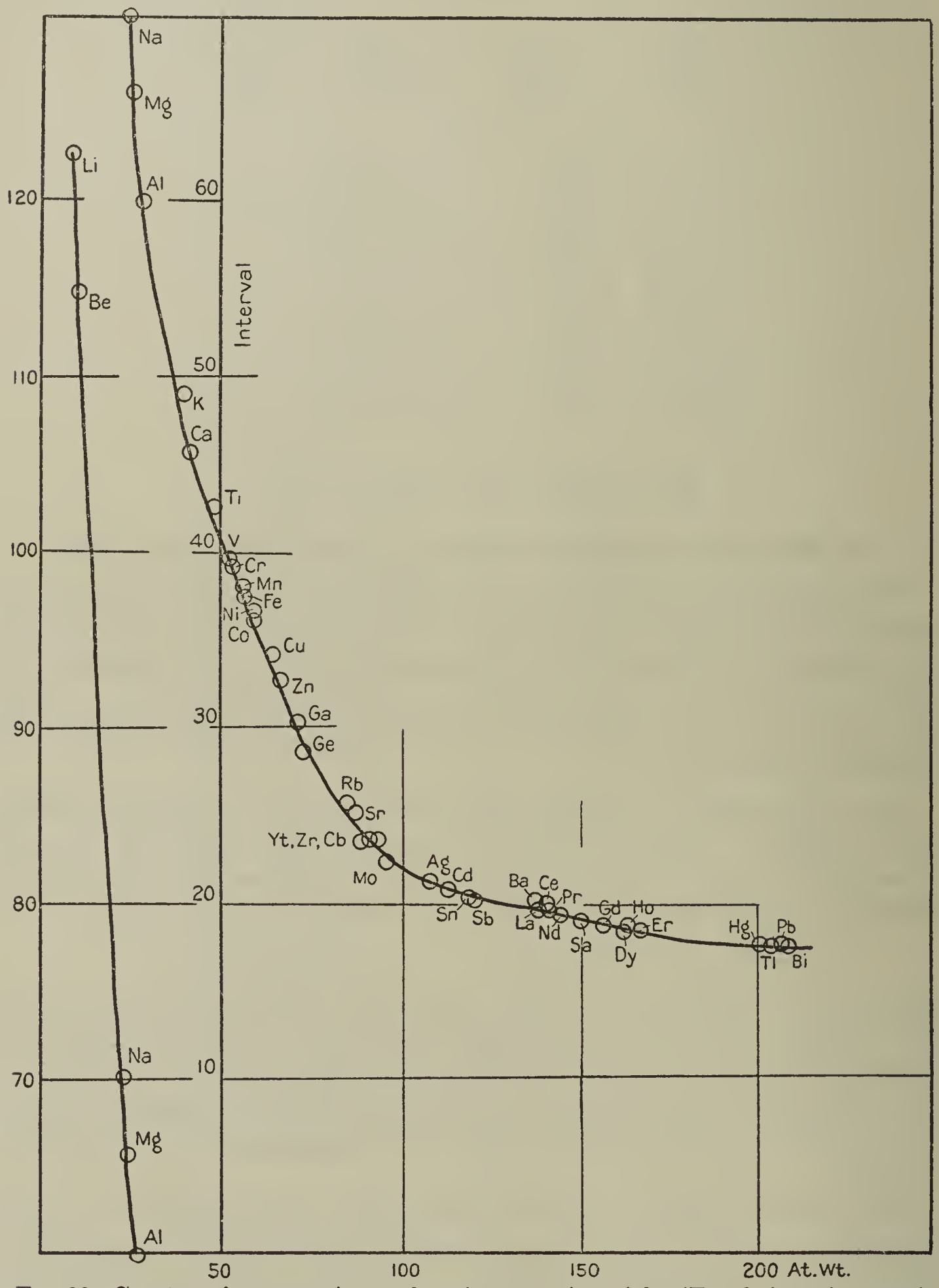


FIG. 26—Constant frequency interval against atomic weight (Tanaka's main curve)

(2) In a solid solution of aluminum sulphate in calcium fluoride, in which the ratio of the atoms of calcium to those of aluminum was 250 : 1, several unknown bands were found, besides those due to

aluminum. The same method as used above suggested that these were due to iron. To test this, the same sample of aluminum salt was mixed with an equal quantity of calcium fluoride, in such a manner that the atoms of calcium and aluminum were in the ratio of 100 : 23. Then, owing to the concentration, no band of aluminum was found, but the unknown bands appeared clearly. A later study of the iron bands showed that these unknown bands must have been due, as was supposed, to an iron impurity present in the aluminum salt. In such a solution the iron seems to be quite active. Chemical analysis of this sample of aluminum salt by its maker showed the presence of 0.005 per cent of iron. According to this, in the first experiment, the ratio of the atoms of iron and calcium was about 1 : 800,000. Luminescence of a solution with such a degree of concentration is often observable.

(3) By the same principle, traces of gallium were found in the same sample of aluminum salt before the bands of gallium were studied.

(4) In several samples of zinc sulphide, unknown luminescence bands occurred, constituting three sets. Upon consulting the curve $y=f(\mu)$, as above, it was seen that one of the sets must have been due to thallium and the other two to ytterbium. A subsequent study of thallium confirmed the identity of the first set. Ytterbium was not at the author's disposal, so the question of the remaining two sets was undecided, though considering the correctness of previous deductions, it seems probable that they were indeed due to ytterbium. A detailed discussion of this question is given in the next chapter.

Of course, in these determinations the probability of the occurrence of metals was taken into consideration, as well as the position of the mean interval on the curve $y=f(\mu)$.

The anomalous sets mentioned in previous sections were not found in any of the solid solutions studied in this section. They must be of very rare occurrence. This fact greatly facilitated the study to be described in the next chapter.

SUMMARY OF CHAPTER III

(1) The cathodo-luminescence spectra of 129 solid solutions, with 42 metals as active agents, were studied spectrophotometrically.

(2) Whatever bases are used, each dissolved metal shows its characteristic luminescence, though this is often very faint.

(3) Each luminescence spectrum is composed of several sets of overlapping bands, each set spaced equally in frequency units.

(4) Each metal has in most cases two, but sometimes four, rarely one or three, sets characteristic of it.

(5) In very rare cases anomalous sets occur besides these (see the summary to Section II).

(6) Such characteristic sets were determined for 42 metals.

(7) For each metal there exist two characteristic frequency intervals, different or coincident; these intervals are totally independent of the properties of solvents.

(8) The average of these two intervals decreases quite regularly with the increase of the atomic weight of the metal.

(9) Of the metals studied, those having comparatively high luminescent powers are the active metals of Lenard and Klatt's sulphides, and gallium, praseodymium, samarium, dysprosium, erbium, etc.

CHAPTER IV

ON THE ACTIVE AGENTS OF SOME LUMINESCENT SUBSTANCES[1]

(Describing further experiments by Mr. T. Tanaka)

I. CALCITES, ARAGONITES, AND DOLOMITES

In his study of the cathodo-luminescence of solid solutions of 42 metals (Chapter III of this treatise), the author determined the location of the luminescence bands characteristic of those metals, the frequency intervals of each one, and certain regular relations existing between these frequency intervals and the atomic weight.

These results give a principle by which the identity of a metal to which certain bands are known to be due can be ascertained, and by using this principle the author has investigated some luminescent substances the active agents of which have long been subjects of discussion. In the following pages the cathodo-luminescence of certain calcites and related minerals will be considered. Most of these were furnished by the department of mineralogy of Cornell University, through the kindness of Professor Gill, to whom the author is especially indebted.

The study of the luminescence of calcites has a long history. It can be traced back to the work of Becquerel, beginning in 1859.[2] In his later experiments Becquerel[3] found that the luminescent samples of calcite contained a fair quantity of manganese (up to 2.7 per cent), while less brilliant samples contained manganese in very small proportions, or not at all, so far as ordinary chemical methods could determine. He[4] also mentions that, to produce luminescence in a marked degree, a few per cent of salts of some alkaline metals, as sodium, lithium, or rubidium, must be present. This action of alkaline metals may be analogous to that of fluxes in Lenard and Klatt's sulphides.

More recently, Headden[5] made precise chemical analyses of several samples of calcite. He found in each sample a few hundredths of 1 per cent of the rare-earth metals, and noticed that, in strongly

[1] T. Tanaka. Jour. Opt. Soc. Am., v. VIII, p. 411, v. VIII, p. 501, v. VIII, p. 659. (1924.)

[2] E. Becquerel. Ann. de Chimie et de Physique (3), 57, p. 40, 1859.

[3] *Ibid.* Comptes Rendus, 103, p. 1098, 1886.

[4] *Ibid.* 107, p. 892-895; 1889.

[5] W. T. Headden. Am. Jour. of Science (4), 21, p. 301-306, 1906.

luminescent calcites, the ratio of yttrium oxides to cerium oxides was a few times greater than in samples of feebly or non-luminescent calcites. Hence he was inclined to attribute the effect to salts of the yttrium group. But it seems unlikely to the present author that so small a change in the concentration of the active agent should produce an essential change in the luminescence. Such a result is inconsistent with facts previously discovered experimentally. For example, according to Bruninghaus's experiment[1] the increase of MnO dissolved in CaO from 0.01 per cent to 0.10 per cent changes the intensity of cathodo-luminescence only from 7 to 9.

Quite recently, Nichols, Howes and Wilber[2] (see Chapter II) studied the cathodo-luminescence of calcites, some of which were the same samples that are here studied in further detail. In conformance with Becquerel's opinion, they attributed the luminescence of calcites to traces of manganese salts present in them. This investigation may be regarded as a continuation of their researches.

In the case of each sample, the positions of the luminescence bands present were determined by repeated experiments. Each band thus located was then found to be, within the limits of error in measurements, identical with some band of one of the metals whose characteristic luminescence bands had been previously determined.[3]

In the following tables the wave-lengths of the crests in the spectrum of the sample studied are given in Ångström units. Where the readings do not coincide with those for the corresponding metal crest, as determined in the investigation just cited, the discrepancy is indicated; *e. g.*, 5795(4), which means that while the reading for the calcite crest was 5795, that of the crest with which it is identified was given as 5794.

TABLE X—*Calcites*

Substance	Active agents	Bands identified
Calcite I.....	Mn(12)	5910, 5893(6), 5831, 5795(4), 5754, 5690(1), 5617(8), 5573(4) 5524(5), 5469(70), 5423, 5367(5)
	Dy(3)	5872(3), 5719(20), 5659(61)
Calcite II....	Mn(7)	5855, 5896, 5794, 5523(5), 5489(8), 5432, 5423
	Yt(6)	6133(5), 5817, 5762(3), 5669(70), 5599, 5531
	Tl(3)	6075(3), 6010, 5710(1)
Calcite III....	Mn(9)	5897(6), 5855, 5831, 5793(4), 5742(1), 5681(2), 5632(1), 5558(9), 5524(5)
	Dy(4)	5871(3), 5781(0), 5720, 5603

[1] M. L. Bruninghaus. Comptes Rendus, 144, p. 839, 1907.
[2] Nichols, Howes and Wilber. Physical Review (2), 12, p. 351, 1918.
[3] Tanaka. J. O. S. A. and R. S. I., 8, p. 287; 1924. The table is reprinted in this treatise, pp. 47-57.

TABLE X—*Calcites*—Continued

Substance	Active agent	Bands identified
Calcite IV....	Mn(10)	6161(58), 6127(31), 5896, 5853(5), 5834(1), 5794, 5755(4), 5740(1), 5681(2), 5618
	Yt(6)	6053, 6017(6), 5972, 5929, 5820(17), 5670
	Dy(4)	5938(6), 5875(3), 5781(0), 5718(20)
Calcite V.....	Mn(11)	6202(3), 6157(8), 6130(1), 5977, 5910, 5893(6), 5830(1), 5794, 5741, 5689(91), 5616(8)
	Yt(4)	6104(5), 6053, 5929, 5669(70)
	Tl(3)	5948, 5771(69), 5710(1)
	Dy(1)	5873
Calcite VI....	Mn(12)	6031, 5977, 5973(4), 5910, 5830(1), 5795(4), 5755(4), 5739(41), 5692(1), 5680(2), 5631, 5559
	Yb?(7)	5962(4), 5865(6), 5776, 5717(6), 5598(9), 5577, 5522
Calcite VII...	Mn(13)	6427, 6291(3), 6225(7), 6202(3), 6158, 6128(31), 6099(8), 5894(6), 5853(5), 5753(4), 5740(1), 5691, 5631
	Dy(5)	6383(5), 6272(5), 6069(8), 5809(11), 5659(61)
	Sa(3)	6041, 6019(7), 5966
Calcite VIII..	Mn(9)	6426(7), 6361, 6286(9), 6129(31), 6044(6), 5981(77), 5898(6), 5853(5), 5683(2)
	Yt(3)	6491, 6199(7), 5743(2)
Calcite IX....	Mn(15)	6544, 6502, 6462(4), 6427, 6360(1), 6288(9), 6204(3), 6132, 6095(8), 5979(7), 5852(5), 5793(4), 5753(4), 5690(1), 5631
	Yt(2)	6053, 5928(9)
Calcite X.....	Mn(19)	6545(4), 6464, 6426(7), 6360(1), 6225(7), 6201(3), 6159(8), 6129(31), 6099(8), 6048(6), 5980(77), 5973(4), 5909(10), 5794, 5752(4), 5680(2), 5630(1), 5575(4), 5523(5)
	Dy(2)	6275, 5844(2)
Calcite XI....	Mn(13)	6503(2), 6427, 6292(3), 6228(7), 6159(8), 6097(8), 6047(6), 5977, 5896, 5854(5), 5755(4), 5693(1), 5631
	Dy(5)	6422, 6348, 6001, 5934(6), 5809(11)
Calcite XII...	Mn(10)	6359(61), 6202(3), 6157(8), 6098, 5977, 5910, 5795(4), 5741, 5680(2), 5621(18)
	Sa(6)	6533(4), 6444(6), 6269, 6120(18), 6039(41), 5841

NOTES ON TABLE X

CALCITE I (from Crugers, Westchester County, New York)—Luminescence orange of medium intensity. Twelve manganese and three dysprosium bands were recognized.

Dysprosium is a rare-earth metal belonging to the yttrium group. It is well known that yttrium is of very frequent occurrence in calcium minerals, and that it is almost always associated with traces of other members of its group. Furthermore, it was found by the author in the studies previously described that, in calcium carbonate as solvent, dysprosium is one of the active agents producing the greatest luminescence, the color being orange. Therefore the participation of dysprosium in the luminescence of this sample of calcite is quite probable, while it would be difficult to explain such a luminescence spectrum by the occurrence of yttrium, samarium, thallium, cerium, or some other metal.

It need hardly be said that almost all samples of calcite contain manganese salts, and that manganese dissolved in calcium carbonate is a very prominent active agent. Other probable impurities of calcite, discoverable by ordinary chemical analysis, are iron, magnesium and zinc, but these are by no means prominent active agents, as may be seen by referring to the paper already cited. The luminescence of this calcite, however, should doubtless be attributed chiefly to manganese, especially as the pres-

ence of a small quantity of that metal in the sample was also proved by Volhard's reaction.

CALCITE II (from Mahopac Mines, Putnam County, New York)—Luminescence orange but quite faint. Seven manganese, six yttrium, and three thallium bands were recognized.

Since the manganese bands are abundant in the region of smaller brightness, the chief effect is to be attributed both to yttrium and to manganese, while thallium plays some part. The wide distribution of yttrium and thallium is generally recognized, so that their occurrence in the calcite is not surprising. By Volhard's reaction only faint traces of manganese could be detected.

CALCITE III (from Tompkins Cove, Westchester County, New York)—It showed a luminescence of medium intensity, and a sharp spectrum curve with well-defined subordinate crests was obtained. Nine manganese and four dysprosium bands were recognized. The probability of the occurrence of dysprosium has already been discussed in the case of Calcite I. By Volhard's reaction the presence of a fair quantity of manganese in the present sample was detected; hence the chief effect in this case is doubtless due to that metal.

CALCITE IV (from the Tungsten Mine, Long Hill, Connecticut)—It showed a somewhat faint luminescence, and a spectrum curve with a rather broad summit was obtained. Ten manganese, six yttrium, and four dysprosium bands were found. The chief effect is to be attributed to manganese and yttrium, while dysprosium plays a less important part.

By Volhard's reaction the presence of a comparatively large quantity of manganese was detected in this sample, yet the luminescence was rather faint in comparison with that of other samples containing less manganese. It is not reasonable to attribute this fact to a too great concentration of manganese, because, according to the researches of Bruninghaus,[1] in order to destroy the luminescence of a mixture of calcium carbonate with a manganese salt the manganese must increase to 10 per cent or more. The faintness may be due to (1) the absence of alkaline metals whose presence would be favorable to the phenomenon, (2) the presence of some other metal or metals, whose presence is unfavorable to it, or (3) failure to have received some natural treatment which, perhaps, the substance must undergo in order to show high luminescent power. The presence of yttrium in samples of fluorspar from the same locality was reported by Humphreys.[2]

CALCITE V (from Mahopac Mines, Putnam County, New York)—This sample was from the same locality as Calcite II. Nevertheless, it showed a fairly bright luminescence. Eleven manganese, four yttrium, and three thallium bands were found; also one dysprosium band.

It may not seem safe to assert the occurrence of dysprosium from the presence of one band only; however, a sharp band with its crest at 6,001 (the location of the crest of one of the dysprosium bands given in table 56 of the previous paper already cited) appeared at one time while working with this calcite. This band was eliminated from the table for Calcite V, because it did not occur steadily; but its appearance may serve to confirm the supposition that dysprosium is present.

Volhard's reaction proved the presence of a fair quantity of manganese, probably the chief active agent in this sample. The active agents are the same as those in Calcite II, which is natural, as the two came from the same locality. The difference in the intensity of the luminescent light is due to the difference in the quantities of manganese contained in them.

CALCITE VI (from Bear Mountain, Rockland County, New York)—Luminescence of medium intensity. Twelve bands due to manganese were found, with seven due to an unknown element, which must be the same as that found in the study of the zinc sulphides to be described in a forthcoming paper. This was supposed to be ytterbium, a rare-earth metal of such wide distribution that its occurrence in this sample would not be surprising. The presence of a fair quantity of manganese in the sample was detected by Volhard's reaction.

CALCITE VII (from Cumberland, England)—Luminescence a fairly bright reddish orange. Thirteen manganese, five dysprosium, and three samarium bands were found. The presence of a small quantity of manganese was also proved by Volhard's reaction. Humphreys has shown that many samples of fluorspar from the same locality contain fair quantities of yttrium, but careful studies of the spectrum curve in this case failed to disclose a single band due to that element.

[1] M. L. Burninghaus. Comptes Rendus, 144, p. 839, 1907.
[2] W. J. Humphreys. Astrophysical Journal, 20, pp. 266-273, 1904.

Calcite VIII (from Colorado)—Luminescence a rather faint orange; spectrum curve beautifully jagged. Nine manganese and three yttrium bands were detected. This sample and the next were furnished by Professor W. P. Headden. He mentions them in his paper[1] as "yellow, strongly phosphorescent calcites" and proved by a careful chemical analysis the presence of comparatively large quantities of yttrium. But while some yttrium bands appear, yttrium certainly can not be the chief active agent of the luminescence. The presence of a small quantity of manganese was detected by Volhard's reaction.

Calcite IX—This sample came from the same locality as calcite VIII, and showed a similar, though somewhat brighter, luminescence. Fifteen manganese and two yttrium bands were found. The result is in every way similar to that of calcite VIII. The presence of manganese was detected by Volhard's reaction.

Calcite X (from Franklin Furnace, New Jersey)—Luminescence very bright reddish orange; spectrum curve jagged. Nineteen manganese and two dysprosium bands were found. The presence of a fair quantity of manganese was detected by Volhard's reaction.

Calcite XI (from Lowville, New York)—Luminescence very bright. Spectrum curve quite similar to that of calcite X. Thirteen manganese and five dysprosium bands were found. The presence of a fair quantity of manganese could be detected by Volhard's reaction.

Calcite XII—This sample was taken out of an old Crookes tube. It showed a reddish orange luminescence of medium intensity. Ten manganese and six samarium bands were found. The presence of manganese could be detected by Volhard's reaction. The occurrence of samarium may be regarded as probable, since samarium, which shows a prominent luminescence in the orange region similar to that of manganese, is a widely distributed element.

Calcite XIII—The origin of this and of the remaining six samples of calcites is unknown. In this case twelve manganese and three thallium bands were identified, in the region 6,300 to 5,600. The intensity of luminescence was rather faint. The presence of traces of manganese was shown by Volhard's reaction.

Calcite XIV—Fourteen manganese and five dysprosium bands were identified, in the region 6,500 to 5,500. The luminescence was very bright. The presence of manganese was shown by Volhard's reaction.

Calcite XV—The luminescence was so faint that the author found it necessary to accustom his eye to darkness for about fifteen minutes before he could make any measurements. Eleven bands of strontium and two of cerium were identified in the region 5,265 to 5,125. The luminescent color was greenish white, differing from that of the other calcites studied. No manganese could be detected by Volhard's reaction.

Calcite XVI—Nine manganese and three dysprosium bands were found in the region 6,360 to 5,690. The presence of manganese could be detected by Volhard's reaction.

Calcite XVII—Nine manganese and three yttrium bands were identified, in the region 6,500 to 5,500.

Calcite XVIII—Twenty manganese bands were found, in the region 6,675 to 5,450. No bands due to other metals appeared.

Calcite XIX—Fifteen manganese and four yttrium bands were identified, in the region 6,600 to 5,450.

Table XI—*Limestones, aragonites, etc.*

Substance	Active agent	Bands recognized
Crystalline limestone I:	Dy(11)	6100(1), 6001, 5907(5), 5873, 5810(1), 5780, 5749(50), 5720, 5690(1), 5660(1), 5632
Red band	Mn(7)	6048(6), 5978(7), 5895(6), 5855, 5752(4), 5559, 5430(2)
	Tl(4)	5951(48), 5884(7), 5711, 5602(0)
Blue band	Dy(7)	4970, 4944(7), 4925, 4900(3), 4885(2), 4838(9), 4798(6)
	Mn(2)	5005, 4885(3)

[1] W. P. Headden. American Journal Science, (4), 21, pp. 301-306, 1906.

TABLE XI—*Limestones, aragonites, etc.*—Continued

Substance	Active agent	Bands recognized
Crystalline limestone II.	Mn(8)	5896, 5858(5), 5834(1), 5794, 5740(1), 5693(1), 5631, 5616(8)
	Dy(6)	5998(01), 5811, 5779(80), 5722(0), 5661, 5603
	Tl(2)	5947(8), 5657(5)
Old lime.....	Mn(12)	6361, 6288(9), 6228(7), 6158, 6099(8), 6048(6), 5974, 5911(0), 5752(4), 5691, 5628(1), 5574
	Dy(2)	5845(2), 5812(1)
Aragonite I...	Mn(17)	6227, 6157(8), 6100(98), 6029(31), 5974, 5910, 5893(6), 5857(5), 5831, 5794, 5754, 5741, 5682, 5632(1), 5560(59), 5470, 5423
	Sr(3)	5961(59), 5818(6), 5504(6)
Aragonite II..	Sr(32)	5771(0), 5718(9), 5680, 5636, 5610, 5576(5), 5550, 5540, 5509(8), 5472, 5440(39), 5406, 5386(5), 5374(3), 5347(6), 5340(1), 5308(7), 5265(8), 5245(6), 5230(1), 5193, 5186(5), 5154(5), 5125, 5096, 5084, 5050(49), 5039(8), 5014, 5009(10), 4980, 4954
	Cu(2)	5485, 5435
Dolomite I...	Dy(15)	6001, 5933(6), 5873, 5750, 5662(1), 5634(2), 5601(3), 5547, 5518(9), 5410, 5383(4), 5332, 5305(6), 5255, 5205
	Mn(9)	5971(4), 5894(6), 5829(31), 5792(4), 5682, 5572(4), 5487(8), 5469(0), 5421(3)
Dolomite II...	Mn(16)	6542(4), 6462(4), 6369, 6293, 6227, 6160(58), 6100(98), 5973(4), 5894(6), 5831, 5796(4), 5739(1), 5682, 5628(1), 5574, 5523(5)
	Yt(1)	6054(3)
Magnesite....	Mn(10)	6543(4), 6461(4), 6290(3), 6206(3), 6131, 6046, 5979(7), 5910, 5855, 5794
	Dy(3)	6384(5), 6068, 5842

NOTES ON TABLE XI

CRYSTALLINE LIMESTONE I (from Amawalk, Westchester County, New York)—Luminescence of medium intensity. Eleven dysprosium, seven manganese, and four thallium bands were identified.

Only a trace of manganese was shown by Volhard's reaction, though the manganese bands appearing in the spectrum were quite bright. The failure of Volhard's test may not mean a real scantiness of manganese, since the presence of chloride prevents the formation of permanganic acid, upon which this method of detection depends.

A fair amount of dysprosium seems to have been present, since in the case of this sample dysprosium plays a more important part in the presence of the faint blue band whose components are given in the second part of the table for this sample. The occurrence of a blue band similar to this was very clearly recognized in the author's experiment upon a solid solution of dysprosium in calcium carbonate.

CRYSTALLINE LIMESTONE II (from Verplanck's Point, Westchester County, New York)—Luminescence rather faint. Eight manganese, six dysprosium, and two thallium bands were identified. The presence of a fair amount of manganese was detected by Volhard's reaction.

OLD LIME—This sample was from cylinders originally prepared for a lime light. When first tried it was almost inactive, but after being heated to a red glow for about 30 minutes it became highly luminescent. The envelope of its spectrum curve had its maximum at about 5,950 Å. U. Twelve manganese and two dysprosium bands were recognized. The presence of a small quantity of manganese was detected by Volhard's reaction.

ARAGONITE I—This sample consisted of fine powder taken out of an old Crookes tube and showed a brilliant orange luminescence, very similar to that of calcite XII. Seventeen manganese and three strontium bands were identified. The presence of a small quantity of manganese was detected by Volhard's reaction.

ARAGONITE II—This sample came from Arizona. It showed a beautiful green lumi-

nescence in the early stages of the cathode-ray bombardments, but after about 10 minutes this turned to a faint whitish color. The appearance was entirely different from that of the previous sample. Thirty-two strontium and two copper bands were found.

The frequent occurrence of traces of strontium in aragonites has been known for a long time. Indeed, for many years previous to the date of the discovery of the law of dimorphism, the difference between the crystalline forms of calcite and aragonite was believed to be due to the presence of strontium salts in the aragonite. Becquerel[1] described aragonite as a mineral showing a greenish blue luminescence, which did not change its color when the mineral was transformed into calcite by being heated. He attributed the difference of the luminescent colors of aragonite and calcite to the presence of strontium in the aragonite. But later[2] he seems to have believed it possible that the crystalline form altered the luminescence, since every sample of aragonite studied by him showed a green instead of an orange color. The present result confirms his earlier opinion.

The presence of copper in this sample was confirmed by ordinary chemical analysis, and the blue tint of its natural color is believed to be due to the presence of this metal. But the copper does not play any great part in the luminescence. Volhard's reaction did not detect the presence of any manganese.

Dolomite I (from the Tilly Foster Mine, Putnam County, New York)—Luminescence orange, rather faint. Fifteen dysprosium and nine manganese bands were recognized.

This case was an exception, in that dysprosium was a more important agent of luminescence than was manganese. By Volhard's reaction the presence of a fair amount of manganese was detected. In all five cases, in which manganese did not show a prominent luminescent power in comparison with other agents, namely, in calcite II, calcite IV, calcite XV, crystalline limestone I, and this sample of dolomite, the luminescence was quite faint.

Dolomite II—(from Neusinshan, Manchuria, China)—Luminescence of medium intensity, the spectrum curve forming a broad summit. This seems to be a characteristic of dolomites. Sixteen manganese bands and one yttrium band were found. Of course, the presence of yttrium in such a case is subject to doubt. A small quantity of manganese was detected by Volhard's reaction.

The probable impurities of dolomites, as determined by ordinary chemical analyses, are the same as those of calcites, so that no additional discussion will be necessary here.

Magnesite (from Neusinshan, Manchuria, China)—Luminescence red and of medium intensity. The envelope of its spectrum curve showed a well-defined maximum at about 6,450. Ten manganese and three dysprosium bands were identified. The presence of a small quantity of manganese was detected by Volhard's reaction.

SUMMARY OF THE EXPERIMENTS ON CALCITES

(1) The chief active agent in the luminescence of calcites, crystalline limestones, and dolomites is in most cases manganese, and their luminescent color is orange or reddish orange.

(2) Sometimes manganese does not show a prominent luminescent power; and in such cases the luminescence is generally faint.

(3) Sometimes strontium acts as the chief active agent, giving a greenish, comparatively faint luminescence; such cases occur frequently in aragonites.

(4) Other active agents are dysprosium, yttrium, thallium, and samarium.

II. FLUORSPARS[3]

Fluorspars are often found in a quite pure state, and there is no one impurity almost inevitably present in them, such as manganese

[1] Becquerel. La Lumiere, 1, p. 354, 1867.
[2] *Ibid.* Comptes Rendus, 53, p. 23, 1886.
[3] For other studies of fluorspar see Chapter V.

in the calcites and chromium in alumina. Very careful chemical or spectral analyses often fail to detect the presence of any trace of manganese in luminescent fluorspars. Nevertheless, some authors attribute the continuous luminescence in the green region, which occurs in some samples, to that metal. Magnesium, aluminum, iron, sodium, etc., may occur as impurities in fluorspars, but their luminescent power is too low for them to be considered as the chief active agents. Therefore the active agent must be some element having a high luminescent power, and which is contained in so minute a quantity that it escapes detection by ordinary analyses, probably some rare-earth metal.

The wide distribution of yttrium in minerals has been repeatedly mentioned by Crookes, while Humphreys,[1] by spectral analyses, found that of 129 samples of fluorspar examined by him, 117 contained yttrium and 27 ytterbium. Morse,[2] who examined the fluorescence spectra of some samples of fluorspar, tried in vain to find any systematic occurrence of the bands when the sample was excited by different kinds of electric spark. Next he studied the thermo-luminescence spectra of two samples of chlorophane[3] (a strongly thermo-luminescent variety of fluorspar), and found that they coincided. He tried to find some relation between these spectra and that supposed by Crookes to be due to yttrium, but without success. Urbain[4] studied the solid solutions of many rare earths and determined their characteristic bands. Comparing these with the spectra of some samples of fluorspar, he arrived at the following conclusions: (1) Two samples of fluorspar showing green luminescence have ytterbium as the active agent; one sample showing red luminescence has praseodymium as active agent; one sample showing rosy-white luminescence has samarium and dysprosium as active agents. (2) The luminescence of a certain sample of chlorophane can be explained as the superposition of spectra due to samarium, ytterbium, dysprosium, and gadolinium. The recognition of so many metals as chief agents of the luminescence of fluorspars is not unreasonable; it is an old saying that every element could be detected everywhere had we sufficiently delicate tests for it. At any rate, the whole question must be said to have been left undecided.

Although in most samples of fluorspar the perceptible spectrum extends into the violet, bands in that region are not included in the following table. As we approach the violet end of the spectrum, on account of the decreased sensibility of the eye and the increased dispersion observations are difficult; and moreover, the crowding of the

[1] W. J. Humphreys. Astrophys. Jour., 20, p. 266–273, 1904, and 22, p. 159 (1905).
[2] H. W. Morse. Astrophys. Journ., 21, p. 85-100, 1905.
[3] *Ibid.*, p. 410–417, 1905.
[4] Urbain. Ann. de Chim. et Phys. 5, 18, p. 222, 1909.

members of the sets characteristic of different metals makes the identification of the origin of any band in this region very uncertain. The violet end of the spectrum is of little use, therefore, for the present purpose, and observations made by the method used in the study of calcite were restricted to other portions of the spectrum.

Throughout the tables, the wave-lengths of the crests in the spectrum of the sample studied are given in Ångström units, while discrepancies between these and the wave-lengths of the crests in the spectrum of the metal with which they are identified are indicated by inserting in brackets the last digit in the wave-length of the metallic band, *e. g.*, 5,793(2). This means that the band characteristic of the active metal is at 5,792, while that in the spectrum of the fluorspar was read as 5,793.

TABLE XII—*Fluorspars*

Substance	Active agent	Bands identified
Fluorspar I...	Sa(14)	5277(5), 5248(0), 5227(9), 5193, 5184(3), 5137, 5082(3), 5029(30), 5010, 4979(8), 4928, 4887, 4848, 4696
	Yt(4)	5386, 5317, 5151(49), 5089(91)
	La(3)	4950, 4792(9), 4721
Fluorspar II..	Sa(18)	5181(3), 5139, 5080(3), 5052, 5030, 5010, 4967(8), 4887, 4828, 4780, 4732(3), 4696, 4661(9), 4623, 4597, 4588, 4551(3), 4519
Fluorspar III..	Sa(17)	5308, 5250, 5193, 5138(9), 5081(3), 5053(2), 5030, 5008(10), 4979(8), 4965(8), 4928(7), 4887, 4847(8), 4807(9), 4778(80), 4733, 4696
	Ce(2)	5159(8), 5114(2)
Fluorspar IV..	Sa(17)	5468, 5429(7), 5364(7), 5325(2), 5183,5140(39), 5031(0), 5009(10), 4929(8), 4847(8), 4827(8), 4808(9), 4781(0), 4696, 4658(9), 4550(3), 4511
	Yt(6)	5399(7), 5270, 5090(1), 4767(6), 4715(6), 4619
	La(2)	4950, 4745
	Yb?(1)	5330(28)
Fluorspar V...	Sa(23)	5470(8), 5418, 5368(0), 5308, 5275, 5231(29), 5141(39), 5138(7), 5098(5), 5085(3), 5052, 5030, 5010, 4978, 4967(8), 4925(8), 4876(7), 4808(9), 4733, 4685(7), 4639(41), 4587(8), 4509(11)
	Mn(2)	4919(21), 4541
	Yt(2)	4764(3), 4716
Fluorspar VI..	Sa(20)	5307(8), 5274(5), 5082(3), 5052, 5030, 5014(0), 4978, 4928, 4890(87), 4851(48), 4831(28), 4809, 4780, 4731(3), 4639(41), 4597, 4553, 4509(11), 4485, 4426(8)
	La(3)	5074(5), 4997(9), 4951(0)
	Yt(2)	5149, 5115(8)
Fluorspar VII.	Sa(17)	5489, 5231(29), 5138(7), 5052, 5008(10), 4969(8), 4929(8), 4845(8), 4778(80), 4732(3), 4688(7), 4659, 4624(3), 4595(7), 4555(3), 4510(1), 4451
	Ce(4)	5205(4), 5168(9), 4898(7), 4814(6)
	Yt(2)	5333, 4765(6)
	Yb?(1)	5128(9)

TABLE XII—*Fluorspars*—Continued

Substance	Active agent	Bands identified
Fluorspar VIII	Sa(23)	5465(8), 5418, 5308, 5277(5), 5229, 5184(3), 5137, 5095, 5083, 5031(0), 4967(8), 4927, 4888(7), 4848, 4830(28), 4810(09), 4782(0), 4734(3), 4688(7), 4662(9), 4623, 4556(3), 4519
	Yt(4)	5209, 4992(4), 4716, 4605(3)
	Dy(1)	4753(5)
	Ce(1)	5348
Fluorspar IX..	Sa(13)	5470(68), 5369(70), 5322, 5229, 5183, 5052, 5031(0), 4978, 4927, 4886(7), 4847(8), 4809, 4780
	Dy(2)	5410, 5109
Fluorspar X..	Sa(12)	5420(18), 5373(0), 5308, 5250, 5192(3), 5083, 5032(0), 4976(8), 4828, 4782(0), 4655(9), 4623
	Er(3)	5151, 4943, 4898

NOTES ON TABLE XII

FLUORSPAR I (from Castleton, Derbyshire, England)—Color yellow, luminescence faint violet, fourteen samarium, four yttrium, and three lanthanum bands were identified.

The presence of small quantities of yttrium in some fluorspars from the same locality was proved by Humphreys, hence the appearance of a few yttrium bands is not surprising, though this can not be considered the chief active agent. Lanthanum belongs to the same group as samarium, so their bands might be expected to occur together. The occurrence and luminescent power of samarium will be discussed at the end of this section.

FLUORSPAR II—This sample was furnished by Vassar College. Color bluish green, luminescence a fairly bright violet. Eighteen samarium bands were found. Certain bands due to erbium seemed to occur in an indefinite way, and are not included in the table.

FLUORSPAR III—This sample, like the preceding, was furnished by Vassar College. Color light blue, luminescence a bright indigo. Seventeen samarium and two cerium bands were identified. The presence of cerium in fluorspar is well known.[1]

FLUORSPAR IV (from Weardale, Durham, England)—Color bright violet, luminescence also bright violet. Seventeen samarium, six yttrium, and two lanthanum bands were identified, also one band due to an element which was probably ytterbium. Humphreys proved the presence of a fair amount of yttrium and a small amount of ytterbium in fluorspars from the same locality; but these are certainly far from being the chief agents of luminescence in this case.

FLUORSPAR V (from near Rosiclare, Illinois)—Color light blue, luminescence blue of medium intensity. Twenty-three samarium, two manganese, and two yttrium bands were identified. Humphreys found traces of yttrium in fluorspars from the same locality.

FLUORSPAR VI (from Cumberland, England)—Color purple, luminescence blue of medium intensity. Twenty samarium, three lanthanum, and two yttrium bands were identified. Humphreys found a fair amount of yttrium in fluorspars from this locality, but that metal does not seem to play an important part in the luminescence.

FLUORSPAR VII (from New Hampshire)—Color a beautiful grass-green, luminescence fairly bright and of a light violet color with a blue tint. Seventeen samarium, four cerium, and two yttrium bands were identified, also one band due to an element which is supposed to be ytterbium. Humphreys found a fair amount of yttrium and traces of ytterbium in several grass-green samples of fluorspar from the same locality.

FLUORSPAR VIII—The origin of this and of the succeeding samples of fluorspar is unknown. This sample had a yellow natural color, and showed a fairly bright, light luminescence. Twenty-three samarium and four yttrium bands were identified; also one dysprosium band and one cerium band. The dysprosium band was very sharp and

[1] P. O. Loew. Berichte der Deutschen Chem. Gesellschaft, 14, p. 1144, 1881.

always occurred in every one of the repeated experiments; and the wave-length of its crest was quite different from any due to any other probable agent. Hence the presence of dysprosium may be recognized without any hesitation.

FLUORSPAR IX—Color a yellowish brown, luminescence a green of medium intensity. Thirteen samarium and two dysprosium bands were recognized. The high luminescent power of dysprosium dissolved in calcium fluoride was demonstrated in Chapter III.

FLUORSPAR X—Color violet, luminescence a fairly bright violet. Twelve samarium and three erbium bands were identified. The high luminescent power of erbium was also established in the studies just cited.

FLUORSPAR XI—Color blue, luminescence a fairly bright purple. The spectrum consisted clearly of two groups of bands, one situated in the orange and the other in the blue. These were resolved into thirteen samarium, twelve thallium and five yttrium bands, in the region between 5,800 and 4,600 Å. U. To judge from relative intensity, thallium played rather a more important part in the luminescence than did samarium, in both portions of the spectrum. The general appearance, also, was similiar to that of the spectrum of thallium dissolved in calcium fluoride, as previously studied by the author.

FLUORSPAR XII—Color light blue, luminescence a fairly bright violet. Twenty-one samarium and four thallium bands were identified in the region of 5,625 to 4,700 Å. U. The spectrum consisted of two groups of bands, one being situated in the blue region and the other, quite faint, in the yellow. In this case thallium played no very important part in the phenomenon.

FLUORSPAR XIII—Color a beautiful green, luminescence a fairly bright violet. Twenty-four samarium, seven thallium, and four praseodymium bands were identified in the region 5,600 to 4,600 Å. U. The spectrum was very similar to that of fluorspar XII. The chief active agent was samarium.

FLUORSPAR XIV—Color a light green, luminescence a fairly bright, light violet. Seventeen samarium and eleven thallium bands were identified, also two bands due to an element which is supposed to be ytterbium. The appearance of the spectrum was similar to those of fluorspars XI and XII. The luminescence is to be attributed chiefly to samarium and thallium.

FLUORSPAR XV—Color a light blue, luminescence a violet of medium intensity. Fifteen samarium and nine praseodymium bands, also one thallium band, were identified in the region of 5,500 to 4,700 Å. U. The bands in the yellow region were all faint. Samarium was the chief active agent.

FLUORSPAR XVI—Colorless, luminescence a faint violet. Seventeen samarium, three yttrium, and three gadolinium bands were identified in the region 5,400 to 4,600 Å. U. The chief active agent was doubtless samarium.

FLUORSPAR XVII—White and opaque, luminescence a faint violet. Seventeen samarium, nine manganese, and four cerium bands were identified in the region between 5,500 and 4,600 Å. U. The chief effect is to be attributed to samarium.

The wide distribution of traces of samarium and of yttrium was mentioned again and again by W. Crookes,[1] but the researches of Lecoq, Baur and Marc, et al., proved his reasoning in respect to yttrium to be totally wrong. He believed in the possibility of luminescence in pure rare earths, and observed in his "pure yttrium" a "citron-colored band" which he considered to be characteristic of that metal. He describes especially the spectrum shown by pure ignited yttric sulphate in a radiant-matter tube as "one of the most beautiful objects in the whole range of spectroscopy," and states that that spectrum showed an intensely brilliant citron-colored band. These statements show very clearly that the origin of the "citron-colored band" can not be yttrium. But there is no fault in his reasoning with respect to samarium.[2] He recognized the impossibility of luminescence in

[1] W. Crookes. Chem. News, vol. 49, p. 159-160, 169-171, 181-182, 194-196, 205-208, 1884.

[2] *Ibid.*, 51, p. 301-303, 1885.

pure samarium salts, and mentioned the remarkable sensibility and intensity of luminescence of the solid solutions of samarium. He observed the characteristic orange band in a solution consisting of 1 part of samarium to 1,000,000 parts of calcium.

Considering the wide distribution and high luminescent power of samarium, it is reasonable to attribute the chief effect in the samples of fluorspar so far studied to that element. There was, however, one seeming discrepancy. Calcium fluoride mixed with a small quantity of samarium was proved by Urbain and others[1] to emit a yellowish orange light, and this was the result obtained by the present author in his previous studies, while the luminescent colors of the samples of fluorspar observed in this investigation were violet, blue, or green.

To test the matter further, several small pieces taken from the before-described samples of fluorspar were heated to red heat, and then put into the cathode-ray tube. It was surprising to see that almost all parts of the surfaces of the pieces emitted beautiful orange light, while a few small parts emitted violet, blue, or green lights of varying shades, perhaps because they had been insufficiently heated. This served as a reminder of the sample of calcium fluoride which had been proved to contain a small quantity of samarium, and which, without previous heating, showed a violet luminescence. The effect of heating on the luminescent color of that sample was therefore investigated. After heating in an open crucible with the luminous flame from a Bunsen burner, the luminescence became blue. After heating with a colorless flame from a Bunsen burner, it became greenish blue. Lastly, after heating to red heat with a gas-blowpipe, the luminescence turned a beautiful orange. The bands found in this case belonged to the same series of samarium as those previously observed for this sample. By adding a small quantity of samarium, the luminescent color at each stage of the heating increased perceptibly. After this, the same sample was kept in a closed glass tube for about six months, and was then tested again. It showed a green luminescence. Upon being heated to red heat the luminescence became once more orange.

Several cases are known in which the color of luminescence is entirely changed by changes in concentration and in the previous heat treatment of the substance.[2] Therefore, in many cases the color of luminescence is not a good criterion by which to identify the active agent. The statement may hold good in the case of fluorspars. In the course of slow variations in the physical condition after previous heating, each sample may emit luminescent light of orange, green,

[1] M. G. Urbain. Ann. d. Chim. et d. Phys., 8, 18, p. 222, 1909.

[2] E. Becquerel. Ann Chim. et phys. (3), 55, p. 5–119, 1859. A. Verneuil, C. R. 103, p. 600–603, 1886. E. Wiedemann und G. C. Schmidt, Ann. der Phys. und Chem., 56, p. 201–254, 1895.

blue, or violet, even though violet may be the color corresponding to the most stable state of the substance.

SUMMARY OF THE EXPERIMENTS ON FLUORSPARS

(1) In most samples of fluorspar the chief active agent is samarium.

(2) Other active agents are yttrium, thallium, lanthanum, cerium, probably ytterbium, etc.

(3) The luminescent colors are violet, blue, and green, but these may change to orange when the substance is heated.

III. CORUNDUM AND SPINEL

It has been long known[1] that alumina shows a beautiful crimson fluorescence under the action of light of high refrangibility or of an electric discharge. Concerning the origin of this luminescence, many opinions have been advanced by both physicists and chemists. Among them, Lecoq[2] insisted from first to last that pure alumina is non-luminescent, and that its luminescence is due to the presence of a small quantity of some chromium salt. Becquerel[3] agreed that the addition of a small quantity of some chromium salt increased the red luminescence of alumina, but insisted that pure alumina itself becomes luminescent when heated to a sufficiently high temperature. He considered that the effect of the chromium salt was due to its increasing the absorbing power of the exciting light. Crookes[4] agreed with Becquerel on the whole, and showed that alumina fractionated from chromium with extreme care was luminescent. He carefully determined the lines of the "alumina spectrum," but, later, finding that some crimson lines of his "alumina spectrum" faded when he used a new method of fractionation[5] he recognized that some of the lines, particularly in the deep red, might be due to chromium. After that, Schmidt[6] reached the following conclusions: (1) Carefully purified alumina is non-luminescent. (2) The addition of a small quantity of chromium salt to pure alumina causes the appearance of a red luminescence. Hence that luminescence must be due to chromium. (3) The addition of a small quantity of copper salt to pure alumina causes the appearance of a green luminescence. Hence the green luminescence of alumina obtained by igniting metallic aluminum (which usually contains a small quantity of copper) must be due to that metal. But these researches were qualitative.

[1] E. Becquerel. Ann. de Chim. et Phys. (5), 57, p. 125, 1859, and (5), 62, p. 90, 1861.
[2] Lecoq de Boisbaudran. C. R. 103, p. 1107, 1224-1227, and 104, p. 330-334, 478-482, 554–556, 824–826, 1887.
[3] E. Becquerel. Ann. de Chim. et Phys. (3), 62, p. 90, 1861, and C. R. 104, p. 334-335, 1887.
[4] W. Crookes. Chem. News, 55, p. 25–27, and 56, p. 59–62, 1887.
[5] *Ibid.*, 56, p. 72-74, 1887.
[6] G. C. Schmidt. Ann. d. Phys. u. Chem., 15, p. 622–633, 1904.

The extensive researches of Wiedemann and Schmidt[1] had established the fact that the luminescent color of alumina mixed with Fe_2O_3, CuO, or Mn_2O_3 undergoes essential variation when changes are introduced in the calcination temperature and in the concentration of the active metal. Therefore it does not seem safe in this case to consider the luminescent color as a unique criterion by which to identify the chief active agent.

From the foregoing the following facts may be gathered:

(1) Pure alumina is non-luminescent.

(2) The purification of alumina for this purpose is very difficult. So small a quantity of some impurity that careful chemical analysis can scarcely detect it, may produce a bright luminescence.

(3) There are several adequate methods of purification. Lecoq and Schmidt succeeded in obtaining pure alumina, but Crookes and Becquerel did not.

(4) Some, at least, of the red lines observed by Crookes and Lecoq must be actually due to chromium. Among them,

(i) The doublet at 6,942 and 6,937 Å. U.[2] (its origin seems to have been the chief subject of the long discussion.)

(ii) Line 6,897 Å. U., found by Lecoq[3] in the spectrum of gallium oxides mixed with chromium. It may be identical with the line 6,895 Å. U., found earlier by Crookes.[4]

(iii) Lines 6,707 and 6,598 Å. U., which disappeared from Crookes's spectrum upon more careful fractionation.[5]

Comparing these lines, or, to speak more exactly, centers of bands, with the crests of the bands characteristic of chromium as obtained by the present author, we find:

Crookes or Lecoq	Cr bands, Tanaka	$\lambda_2-\lambda_1$ in Ångström units
	λ_1	λ_2	
(i)	6,942	6,944	2
	6,937	.....	.....
(ii)	6,897	6,897	0
(iii)	6,707	6,701	−6
	6,598	6,605	7

Except for the value 6,937, there is a correspondent for each one. The differences $\lambda_2-\lambda_1$ are not unreasonably large, if we consider that the wave-lengths for (iii) represent the centers of diffused bands. As to 6,937, it may be pointed out that there are series consisting of

[1] E. Wiedemann and G. S. Schmidt. Ann. d. Phys. u. Chem., 56, p. 201-254, 1895.
[2] W. Crookes. Chem. News, 56, p. 56–62, 1887.
[3] Lecoq de Boisbaudran. C. R. 104, p. 1584–1585, 1887.
[4] W. Crookes. Chem. News, 43, p. 237–239, 1881.
[5] *Ibid.*, 56, p. 72-74.

doublets, occurring in zinc sulphate mixed with manganese, of which this may be a member.[1]

Besides these, the following centers of bands in the fractionated alumina spectrum and alumina-samaria spectrum as observed by Crookes[2] correspond closely to certain bands assigned by the present author to chromium:

Crookes	Tanaka	$\lambda_2-\lambda_1$ in Ångström units
λ_1	λ_2	
6,795	6,795	0
6,773	6,773	0
6,514	6,517	3

Many other lines found in Crookes's alumina spectrum must have been due to other sources not eliminated by the fractionation.

TABLE XIII—*Corundum, ruby, and spinel*

Substance	Active agent	Bands identified
Corundum I....	Cr(14)	6306, 6233(5), 6174(6), 6095, 6019, 5942(1), 5900, 5869(70), 5795 (6), 5777(6), 5593(2), 5541(3), 5527(5), 5463
	Sa(12)	6405(3), 6333(6), 6280(78), 6204, 6117(8), 6039(41), 5820(2), 5753(2), 5686(4), 5675, 5622, 5417(8)
	Cu(3)	6374(6), 5987(8), 5925(8)
	Fe(2)	6067(70), 6000(2)
Corundum II....	Cr(9)	5966(4), 5867(70), 5836(7), 5775(6), 5715(6), 5593(2), 5544(3), 5460(3), 5340(9)
	Sa(5)	6041, 5730(29), 5674(5), 5490(89), 5308
	Fe(2)	5624(3), 5504(7)
Artificial ruby...	Mn(12)	5490(88), 5310(1), 5275(4), 5248(7), 5182(1), 5139, 5085(4), 5052(1), 5025, 5004(5), 4979(8), 4883
	Cr(4)	5382(0), 5340(39), 5218(1), 4945(7)
Spinel.....	Mn(13)	5488, 5469(70), 5430(2), 5420(3), 5371, 5309(11), 5274, 5247, 5220, 5183(1), 5142(39), 5084, 5005
	Fe(1)	5343(2)

NOTES ON TABLE XIII

CORUNDUM I (from Craigmont, Renfrew County, Ontario)—It showed a faint greenish luminescence, not sufficiently bright for measurements, so it was ground into a fine powder and heated to red heat for about half an hour. The luminescence then obtained was red. Fourteen chromium, twelve samarium, three copper, and two iron bands were identified. The existence of the band 5,925 is definite evidence for the presence of copper, since this band is not near any band of any other metal which can be expected to occur in corundum.

CORUNDUM II (from Franklin, Macon County, North Carolina)—It, like the preceding, had to be ground into fine powder and heated to a red glow in order to obtain a luminescence of sufficient intensity for measurements. Nine chromium, five samarium, and two iron bands were identified.

[1] Tanaka, l. c.
[2] W. Crookes. Chem. News, 56, p. 59–62, 1887.

According to the results obtained for these two samples, the chief active agents of the luminescence of corundum are chromium and samarium, while iron and sometimes copper plays a small part.

The occurrence of chromium and samarium as impurities in alumina has been recognized by many physicists and chemists, to say nothing of iron, which, of all metals, has the widest distribution. The occurrence of copper in aluminum ores is quite probable also; the metallic aluminum manufactured from such ores (for example that obtained by the electrolysis of the solutions of alumina in fused cryolite, Na_3AlF_6) is known to include, usually, a small quantity of copper.

It is known[1] that alumina mixed with a small quantity of chromium, samarium, iron, or copper, without being calcined, shows a hardly observable or faint greenish luminescence, and that after heating to a red glow it begins to emit a red luminescence. This change is accentuated if the concentration of the active metal is small. Similar variation in luminescence color, upon the process of calcination, is observable in most samples of alumina, corundum, and ruby.[2] It was also true of the two samples of corundum just described.

"Artificial Ruby"—This sample (from Eimer and Amend) was a dark-brown substance with a red tint. It showed a beautiful green luminescence. Twelve manganese and four chromium bands were identified. Manganese must be the chief active agent in this case.

Spinel ($MgO.Al_2O_3$) is a natural magnesium aluminate. It is known that a small part of the MgO is often replaced by MnO or FeO, and a small part of the Al_2O_3 by Cr_2O_3 or Fe_2O_3. Two samples of spinel were at the author's disposal. One of them was a ruby spinel from Ceylon, and was almost non-luminescent in its original state. Since it was a registered article belonging to the department of mineralogy of Cornell University, it could not be calcined, and the present observations are confined to the other sample.

This sample came from Antwerp, New York. It had a white natural color, with a violet tint. Not being sufficiently luminescent, it was ground into fine powder and heated to red heat for about half an hour, when it showed a quite beautiful yellowish-green luminescence. Fifteen manganese bands were identified and one iron band. The iron band might be attributed to chromium, which has a band at 5,539, making $\lambda_2-\lambda_1=-4$. Of course it is difficult to determine the origin of one band alone. But at one time in the experiments with this sample, a crest was found at 5,454, which is reasonably near to an iron crest at 5,451, but not to any crest of manganese or of chromium. Since this band did not occur frequently enough, it was not included in the table, but its appearance is one ground for attributing 5,343 to iron instead of to chromium.

According to Lecoq,[3] most spinels show red luminescence, but some show green; if we make artificial spinels mixed with traces of either manganese and chromium, we get green and red luminescence respectively. Hence he attributed the luminescence of spinels to those two metals, according to its color. The present result confirms his conclusion regarding spinels showing green luminescence.

As regards the other type of spinel, Crookes[4] drew a map of the luminescence spectrum of a sample showing crimson luminescence. Most of the bands he drew were too broad to be identified by the present method, but he mentioned one sharp line with a wave-length of 6,857. The extrapolation of one of the chromium series previously recorded by the present author shows that this is the exact location of one of its members. Thus it is probable that the active agent in spinels showing red luminescence is chromium. This also agrees with Lecoq's conclusion.

IV. ZINC SULPHIDES

It is certainly a difficult problem to determine the chief active agent in the luminescence of zinc sulphide. The probable impurities of zinc ores are very numerous, including as they do the salts of the following metals: Li, Na, Al, Mn, Fe, Co, Cu, Ga, Ge, Mo, Ag, Cd,

[1] E. Wiedemann and G. C. Schmidt. Ann. d. Phys. u. Chem., 56, p. 201-254, 1895.
[2] W. Crookes. Chem. News, 55, p. 25-27, 1886, and E. Becquerel, C. R. 104, p. 554, 1887.
[3] Lecoq de Boisbaudran. C. R. 105, p. 261–262, 1887.
[4] W. Crookes. Chem. News, 55, p. 25-27, 1887.

In, Sn, Sb, the rare earths, Tl, Pb, and Bi. The occurrence of Fe, Cd, Cu, and Mn is known to be very frequent.

Zinc sulphide mixed with a small quantity of manganese shows an orange fluorescence and has tribo-luminescent properties very similar to those of zinc blende, whence Grüne[1] attributed the origin of the luminescence of zinc blende to manganese. Jorrissen and Ringe[2] found that the addition of small quantities of metallic salts produces, in most cases, some variation in the luminescent color of zinc sulphide, and therefore considered it possible that the luminescence is due to some agent or agents in solid solution.

Henry[3] had previously mentioned that the addition of several metals, which were among the probable impurities, prevented the luminescence of zinc sulphide, whence he concluded that the luminescence proceeded from the pure substance. The fact is that the purification is so difficult that non-luminescent zinc sulphide can scarcely be obtained and that the metals shown by ordinary chemical analysis as impurities are not active in the luminescence. Hoffmann and Ducca[4] found that the luminescence shown by zinc ammonium sulphate mixed with a small quantity of manganese chloride became very prominent in the presence of a small amount of NaCl or $MgSO_4$, which must have played a part similar to that of a flux in Lenard and Klatt's sulphides. Recently Dougall, Steward and Wright[5] conducted an exhaustive investigation with "a view to define more clearly the various factors which are concerned in the production of phosphorescent zinc sulphide." They considered it possible that pure zinc sulphide might be luminescent, but according to their observations its power is much weaker than that of "phosphorescent zinc sulphide." Moreover, they found that heating to redness and adding sodium chloride or zinc chloride made the luminescence very prominent, but that the addition of further metals is of no advantage, and that some, indeed, exert a deleterious effect. They seem not to have given any weight to the possibility of active agents in solid solution, and to have attributed the effect, instead, to zinc-sulphide particles covered with thin layers of chloride, fused during calcination. They could find no satisfactory explanation for the change in the luminescent color upon the addition of manganese.

From these researches it would appear that:

(1) The origin of the luminescence of zinc sulphide is probably some agent or agents in solid solution.

[1] H. Grüne. Ber. chem. Ges., 37, 3, pp. 3076-3077, 1904.
[2] W. P. Jorrissen and W. E. Ringe. Fortschritt, 61, 2, p. 486, 1904, and Chem. Zentralbl. (5), 10, p. 1, 64, 1906.
[3] C. Henry. C. R. 115, p. 505, 1892.
[4] K. A. Hoffmann and W. Ducca. Ber. chem. Ges., 37, 3, p. 3407–3411, 1904.
[5] E. M. Dougall, A. W. Steward, R. Wright. Jour. Chem. Soc., 111, pp. 666-683, 1917.

(2) Pure zinc sulphide is almost impossible to obtain, so that even a highly fractionated sample will show a perceptible luminescence.

(3) The chief active agent is probably one which is very difficult to separate from zinc sulphide.

(4) The active agent alone may be unable to produce any prominent luminescence, but may require the presence of some salt as a flux. This action of a flux is well known in the case of Lenard and Klatt's sulphides.

(5) As may be seen in Lenard and Klatt's sulphides, the percentage of the active metal giving maximum brightness of luminescence is exceedingly small, being of the order of 0.01. Therefore traces of an impurity too minute to be detected by accurate chemical analysis may show very remarkable luminescent power.

EXPERIMENTAL RESULTS

Four samples of zinc sulphide were studied, and two samples of zinc blende. In the course of the experiments, which were repeated about 30 times, 48 luminescence bands were found. They belonged to three constant-frequency interval sets, having intervals of 17.4, 17.7, and 18.2 (in 1/Å. U.$\times 10^7$ units) respectively. The bands belonging to the first set coincide in their locations and in their interval with those due to thallium. Since the presence of thallium in zinc sulphides is very frequently shown even by ordinary chemical analysis, the above result is quite to be expected.

The bands of the second set do not seem to belong to any one of the forty-two metals previously studied by the author. The bands belonging to the third set nearly coincide with those belonging to one of the sets due to erbium; but the other erbium set is quite different from anything given by the zinc sulphides. Hence it may be that the approximate coincidence between the third set in this case and one of the erbium sets is only accidental, and that the third set too is due to some other metal not yet studied. Since each rare earth has, in general, two characteristic sets, it may be that both the second and third sets in this case are due to the same metal. Taking the mean value of their intervals, which is 18.0, and looking for some rare earth having this interval-value on the curve given in figure 26, Chapter III, we get *ytterbium.*

The wide distribution of yttrium in minerals was emphatically affirmed by Crookes[1] as the result of his extensive researches; and although the reasoning which brought him to this conclusion has been proved to be wrong, the experimental facts he obtained are of great

[1] W. Crookes. Chemical News, 49, pp. 159-160, 169-171, 181-182, 194-196, 205-208, 1884.

value. According to his experiments, some element showing a bright citron-colored band must exist and must be widely distributed. It can not be yttrium, as Crookes supposed, but it must be something which it is very difficult to separate from yttrium. Crookes's researches show not only the wide distribution of that unknown element, but also of yttrium itself. What was that element? The question seems to be still an open one.

Crookes says in one of his papers:[1]

"Gadolinite was purified from all the earths, whose sulphates are with difficulty soluble in potassium sulphate, then from terbia, and lastly from erbia earths. Now gadolinite contains only about 0.1 per cent of ytterbia, and about 35 per cent of yttria, and it gave the citron band spectrum as brilliantly as I had ever seen it. The probability was that the earth forming nearly the whole was the one giving the spectrum."

According to our present knowledge, this statement shows that the probable active agent was *not yttrium but ytterbium.* The concentration of 0.1 per cent is not far from that which gives the maximum intensity of luminescence for many substances. Crookes says again:

"The precipitate thus obtained with tartaric acid and ammonia should therefore contain all the yttria; it gave no citron band whatever in the radiant-matter tube, whilst the residue, which should be free from yttria, proved for a long time the only source of material wherewith to investigate the chemical properties of the body giving the citron band spectrum."

A too concentrated yttrium solution was not luminescent, and the true active agent had been removed by his method of purification. He says further:

"Pure yttria precipitated by ammonia did not phosphoresce in the slightest degree, and necessarily, no citron band spectrum was to be seen. The yttria was converted into sulphate, heated to redness, and again tested. This time it gave the citron band magnificently."

The first yttria was free from the active agent, but the chemical process must have introduced traces of it. The wide distribution of yttrium and ytterbium has been proved by Humphreys[2] by the analysis of many samples of fluorspar, which nearly always contained yttrium and often ytterbium.

In support of his contention the present author submits the following comparison of Crookes's "yttrium bands"[3] (Cr) and those by himself (T) and assumed by him to be due to ytterbium. The differences are given under Δ, table XIV.

[1] W. Crookes, Chemical News, 49, pp. 205-208, 1884.
[2] W. J. Humphreys. Astrophys. Jour., 20, pp. 266–273, 1904, and 22, p. 157, 1905.
[3] W. Crookes. Chem. News, 56, p. 81-82, 1887.

TABLE XIV

Cr.	T.	Δ	Cr.	T.	Δ	Cr.	T.	Δ	Cr.	T.	Δ
647	647.1	0	603	603.0	0	568	568.9	1	541	541.7	1
639	639.8	1	597	596.4	−1	563	563.3	0	482	481.6	0
619	618.8	0	574[1]	574.7	1	550	548.8	−1	456	457.4	1
609	609.6	1									

[1] The citron band.

The correspondence is good. If Crookes's spectrum is compared, instead, with lanthanum, cerium, praesodymium, neodymium, gadolinium, dysprosium, holmium, erbium, thallium, or yttrium, several of his bands fail to find a corresponding band. Samarium gives the closest comparison, but even with it the deviations are much larger than those in table XIV.

The two sets which are probably due to some one element (ytterbium ?) are shown in table XV:

TABLE XV—*Bands due to an unknown element*

Set I (17.7)				Set II (18.2)			
5928	1686.9	5417	1846.2	5900	1694.9	5380	1858.7
5866	1704.6	5365	1863.9	5837	1713.1	5328	1876.0
5806	1722.3	5315	1881.6	5776	1731.3	5277	1895.1
5747	1740.0	5265	1899.3	5716	1749.5	5227	1913.3
5689	1757.7	5217	1917.0	5657	1767.7	5177	1931.5
5633	1775.4	5169	1934.7	5599	1785.9	5129	1949.7
5577	1793.1	5122	1952.4	5543	1804.1	5082	1967.9
5522	1810.8	5076	1970.1	5488	1822.3	5035	1986.1
5469	1828.5	5031	1987.8	5433	1840.5	.....	.....

In table XVI, the bands which are due to an unknown element, presumably ytterbium, are designated by the letter X.

TABLE XVI—*Sulphides and blendes*

Substance	Active agent	Bands found
Zinc sulphide I....	X(18)	5866, 5805(6), 5745(7), 5686(9), 5634(3), 5595(9), 5574(7), 5525(2), 5487(8), 5414(7), 5312(5), 5274(7), 5220(17), 5177, 5169, 5120(2), 5082, 5035
	Tl(2)	5441, 5338(40)
Zinc sulphide II...	X(18)	5716, 5687(9), 5633, 5602(9), 5575(7), 5520(2), 5433, 5382(0), 5315, 5277, 5265, 5227, 5216(7), 5178(7), 5131(29), 5120(2), 5076, 5033(1).
	Tl(2)	5342(0), 5015(4).
Zinc sulphide III..	X(17)	5864(6), 5806, 5747, 5689, 5630(3), 5574(7), 5520(2), 5470(69), 5415(7), 5364(5), 5315, 5263(5), 5218(7), 5168(9), 5129, 5080(2), 5035

TABLE XVI—*Sulphides and blendes*—Continued

Substance	Active agent	Bands found
Zinc sulphide IV...	X(18)	5925(8), 5809(6), 5747, 5716, 5689, 5633, 5578(7), 5522, 5471(69), 5416(7), 5367(5), 5314(5), 5267(5), 5216(7), 5169, 5123(2), 5075(6), 5032(1)
	Tl(3)	5103, 5058, 5016(4)
Zinc blende I.....	X(17)	5577, 5522, 5469, 5418(7), 5364(5), 5327(8), 5313(5), 5277, 5263(5), 5218(7), 5178(7), 5166(9), 5130(29), 5120(2), 5082, 5035, 4985(6)
	Tl(5)	5431(0), 5103, 4968(70), 4928, 4886
Zinc blende II....	X(9)	5468(9), 5415(7), 5367(5), 5316(5), 5267(5), 5227, 5168(9), 5130(29), 5121(2)
	Tl(6)	5493, 5390, 5340, 5194(5), 5148, 5102(3)

NOTES ON TABLE XVI

ZINC SULPHIDE I—This sample was made by A. Verneuil. It showed a very bright, yellowish-green luminescence, in which were found two bands due to thallium and eighteen due to element X.

ZINC SULPHIDE II—This sample was made by A. M. Rousseau. Its luminescence was similar to that of the first sample. There were found in its spectrum two bands due to thallium and eighteen due to element X.

ZINC SULPHIDE III—This sample's maker is unknown. It showed a less bright luminescence than did samples I and II, but the spectrum curve was beautifully shaped, with a maximum at about 5,350 Å. U. The subordinate crests appeared clearly, and it was very easy to determine their locations. There were seventeen of these crests, all due to element X.

ZINC SULPHIDE IV—This sample was reported by C. W. Waggoner as being non-phosphorescent under photo-excitation. It, however, showed a fairly bright luminescence under bombardment by cathode rays. Its luminescent color changed gradually from yellowish green to green during the course of the bombardment. In its spectrum there appeared three thallium bands, and eighteen bands due to element X. The thallium bands were present only at the farther part of the curve, where it is very low; hence they could have very little effect on the color.

ZINC BLENDE I—This sample came from near Joplin, Missouri. It showed a yellowish-green luminescence, similar to that of the artificial zinc sulphides just described. In its spectrum were found seventeen bands due to element X, and five thallium bands most of which were in the extreme portion of the curve. No difference as to active agent was found between this and the artificial samples.

ZINC BLENDE II—This sample came from Mexico. Its luminescent light was yellowish green, but rather faint. In this case six thallium bands were recognized, and nine bands due to element X. The effect of thallium was not inconsiderable in this sample.

Since there are several important metals besides ytterbium whose series have not yet been investigated, it is impossible to decide with absolute certainty as to the identity of element X. But there is a probability that it is ytterbium.

V. WILLEMITES AND KUNZITES

Willemite is a well-known, strongly luminescent mineral with a composition of Zn_2SiO_4 (zinc orthosilicate). The investigations of J. J. Thomson on positive rays owe their success partly to the existence of this highly luminescent substance. But the origin of its luminescence has been investigated by comparatively few. Its luminescent color is always yellowish green, though its natural color

varies widely. The bands found in the spectrum of this and in that of two samples of Kunzite are given in table XVII.

TABLE XVII—*Willemites and kunzites*

Substance	Active agent	Bands identified
Willemite I.....	Mn(15)	5682, 5620(8), 5525, 5470, 5432, 5366(5), 5322(5), 5275(4), 5221(0), 5180(1), 5131(3), 5082(4), 5049(1), 5004(5), 4919(21)
	Fe(3)	5396, 5038(40), 4950(47)
	Tl(2)	5655, 5600
Willemite II....	Mn(12)	5617(8), 5575(4), 5524(5), 5327(5), 5274, 5218(20), 5180(1), 5139, 5094(2), 5082(4), 5050(1), 5005
	Fe(4)	5504(7), 5451, 5339(2), 5287(9)
	Tl(3)	5439(1), 5390, 5151(8)
Willemite III....	Mn(12)	5682, 5523(5), 5363(5), 5310(1), 5271(4), 5247, 5219(20), 5181, 5141(39), 5095(2), 5052(1), 4978
	Tl(5)	5652(5), 5601(0), 5546, 5147(8), 5016(4)
	Fe(2)	5451, 5397(6)
Willemite IV....	Mn(18)	5682, 5629(31), 5557(9), 5525, 5488, 5424(3), 5370(1), 5325, 5249(7), 5274, 5221(0), 5180(1), 5130(3), 5091(2), 5051, 5024(5), 5007(5), 4921
	Tl(3)	5655, 5600, 5104(3)
	Fe(3)	5451, 5397(6), 5341(2)
Kunzite I.....	Mn(11)	6160(58), 6098, 6045(6), 6031, 5977, 5894(6), 5855, 5754, 5691, 5632(1) 5617(8)
	Sa(2)	6077(8), 5957
	Yb?(7)	5991, 5927(8), 5867(6), 5806, 5776, 5713(6), 5599
Kunzite II.....	Mn(12)	6203, 6158, 6098, 6046, 5977, 5910, 5831, 5796(4), 5741, 5691, 5617(8), 5559
	Sa(4)	6118, 6079(8), 5954(7), 5518
	Tl(1)	5655
	Yb?(3)	5864(6), 5714(6), 5600(599)

NOTES ON TABLE XVII

WILLEMITE I—The origin of this sample is unknown. It had a white natural color and showed a very bright luminescence. The spectrum curve showed many well-defined subordinate crests. As may be seen from the table, fifteen manganese, three iron, and two thallium bands were identified. The occurrence of iron in most willemites is well known. Thallium is widely distributed in the ores of light and heavy metals alike.

WILLEMITE II—This sample came from Franklin Furnace, New Jersey. It had a pink tint in its natural color, but otherwise was similar to Willemite I. As may be seen from the table, twelve manganese, four iron, and three thallium bands were identified.

WILLEMITE III—This sample, like the preceding, came from Franklin Furnace, New Jersey. Except for having a green instead of a pink tint it was similar to the preceding. Twelve manganese, three thallium, and two iron bands were identified. The agreement as to active agents between these three samples was of course to be expected.

WILLEMITE IV—This sample was synthesized by Andrews, and it consisted of a fine white powder. Its method of manufacture was unknown to the present author until after the conclusion of the investigation. Its luminescence spectrum curve was quite similar in form to those of the natural willemites studied, but the intensity of luminescence was somewhat greater. Eighteen manganese, three thallium, and three iron bands were identified. The only difference between this result and those for the natural willemites studied is the greater number of manganese bands.

The occurrence of manganese as an impurity in silicates may be accepted as a matter of course. But as to whether zinc silicate containing traces of manganese can show a green luminescence is not so readily determined. Since pure zinc silicate was not at the author's disposal, he could make no study of this point. But some years ago Bourgougon succeeded in making some samples of artificial willemite, which showed luminescence similar to that of natural willemites. The paper about his work, written by Baskerville[1] is so short that it does not give a clear idea of Bourgougons' methods of manufacture. It seems, however, that the zinc silicate he used had a high degree of purity, so that it showed no luminescence in itself, and that in one sample at least the active agent was manganese oxide, other oxides, if used, playing parts similar to those of the fluxes in Lenard and Klatt's sulphides. If this is correct, it confirms the present result.

The only other alternative is samarium. In the spectral region in question, the samarium bands closely correspond to the manganese bands. Hence the difficulty as to which is the active agent of willemites must be decided by determining which shows the characteristic luminescent color of natural willemites, when it is used as the active agent in zinc silicate.

One sample of zinc silicate was at the author's disposal. It was by no means chemically pure, its coloring being red, and it showed a violet luminescence. The luminescence was not changed by mixing with it a small quantity of manganese oxide. A similar result was reported by Andrews.[2] Agents hindering luminescence due to manganese might be present in the sample. But, after mixing with the zinc silicate a small quantity of samarium, a red luminescence was obtained, which became more and more intense upon raising the temperature of calcination. Moreover, no such red tint was obtained by heating the previously studied samples of willemite. Their luminescence was constantly yellowish green, except in the parts consisting of franklinite, which emitted a red light. This experiment, therefore, points to the conclusion that manganese, not samarium, is to be regarded as the chief active agent in willemites.

After the above conclusion was obtained, the original note about the method of preparation of Willemite IV was found. It says that Andrews prepared that sample by mixing together 100 gr. of zinc sulphide, 50 gr. of silicic acid, and 0.5 gr. of manganese oxide, and heating it to a temperature of 1200°. This confirms the result obtained for sample IV and explains the luminescent color shown by zinc silicate mixed with a small quantity of manganese.

KUNZITE I—Few studies of the origin of the luminescence of this well-known luminescent crystal have been made. The present sample showed a very bright orange luminescence. Its origin was unknown. Eleven manganese and two samarium bands were identified, also seven bands due to an element which is probably ytterbium.

KUNZITE II—This sample came from Sickler's Hill, Pala, California. Like Kunzite I, it showed a very bright orange luminescence. Twelve manganese and four samarium bands were identified, also one thallium band, and three bands belonging to an element which is probably ytterbium.

According to these results, the chief active agent in kunzite is manganese, while ytterbium, samarium, thallium, etc., play lesser parts. Analyses of spodumenes from San Diego County, California, by Schaller; of kunzites from Rincon, California, by Jaeger and Simek, and of "kunzites with a deep lilac color, quite free from flaws," by Davis, etc., all indicate the presence of a few tenths per cent of manganese.

[1] C. Baskerville. Chem. News, 95, p. 255–256, 1907.
[2] W. S. Andrews. Fortschr., 60, 2, p. 567, 1904.

CHAPTER V

PHOTOGRAPHIC STUDIES OF SPECTRAL STRUCTURE

[Based on experiments by J. O. Perrine, P. L. Bayley, L. J. Boardman, Frances G. Wick, P. A. Northrup, and R. M. Fisher]

In spite of several very grave objections, the photographic method of studying spectra has its advantages. Long confined to the recording of line spectra, the application of the photo-electric cell as a substitute for the eye has extended the range of photography to include certain spectrophotometric operations. The advantages just referred to are:

(1) The extension of spectrophotometry to the ultra-violet.

(2) The ability to locate and measure bands too feeble for visual determination.

(3) The securing of a permanent record.

I. EXPERIMENTS OF J. O. PERRINE

About the year 1920 Mr. J. O. Perrine devised a form of microphotometer for measuring the density of photographs of spectra made in the course of his investigation of the fluorescence excited by X-rays. The following quotation is from his description of the apparatus in the *Journal of the Optical Society of America.*[1]

"Figure 27 shows the schematic arrangement of the apparatus. The eyepiece, cross-hair, and objective of the comparator telescope (*T*) were removed, leaving only the telescope tube. A 100-watt single-coil filament lamp at X was mounted on the telescope tube at the upper end. A lens (*L*) placed within the tube focussed the light on a slit at the center of a metal plate fitted in the lower end of the tube. The slit was 0.25 mm. wide and 2 mm. high. The photographic plate whose density distribution was to be found was clamped to the comparator stage. By means of the thumb screw which ordinarily raises and lowers the telescope along its axis, the system consisting of lamp, lens, and slit could be moved as a single unit. The slit was lowered to within 0.5 mm. of the surface of the plate on the comparator stage. The light which was transmitted by the small area of the plate in front of the slit entered the photo-electric cell.

"The Elster and Geitel type of photo-electric cell was first tried, but the leakage current or the so-called dark current was so large that reliable results could not be obtained. The Kunz[2] photo-electric cell was, however, found to be satisfactory. When 120 volts were used the dark current seldom exceeded 2 per cent of the maximum light current and after the circuit had been closed for fifteen minutes it decreased to 0.5 per cent."

[1] Perrine. Jour. Opt. Soc. Am., VIII, p. 381.

With this instrument Perrine examined many substances. The following abstract is from his published paper:[1]

The specimen to be studied was mounted in front of the slit of a small Fuess spectrograph,[2] the quartz optical system of which is indicated in figure 28. The X-ray tube was directly above the specimen and the rays passed through the top of a light-tight box fastened to the end of the collimator. The distance from the specimen to the X-ray target was approximately 12 cm. The plate-holder could be

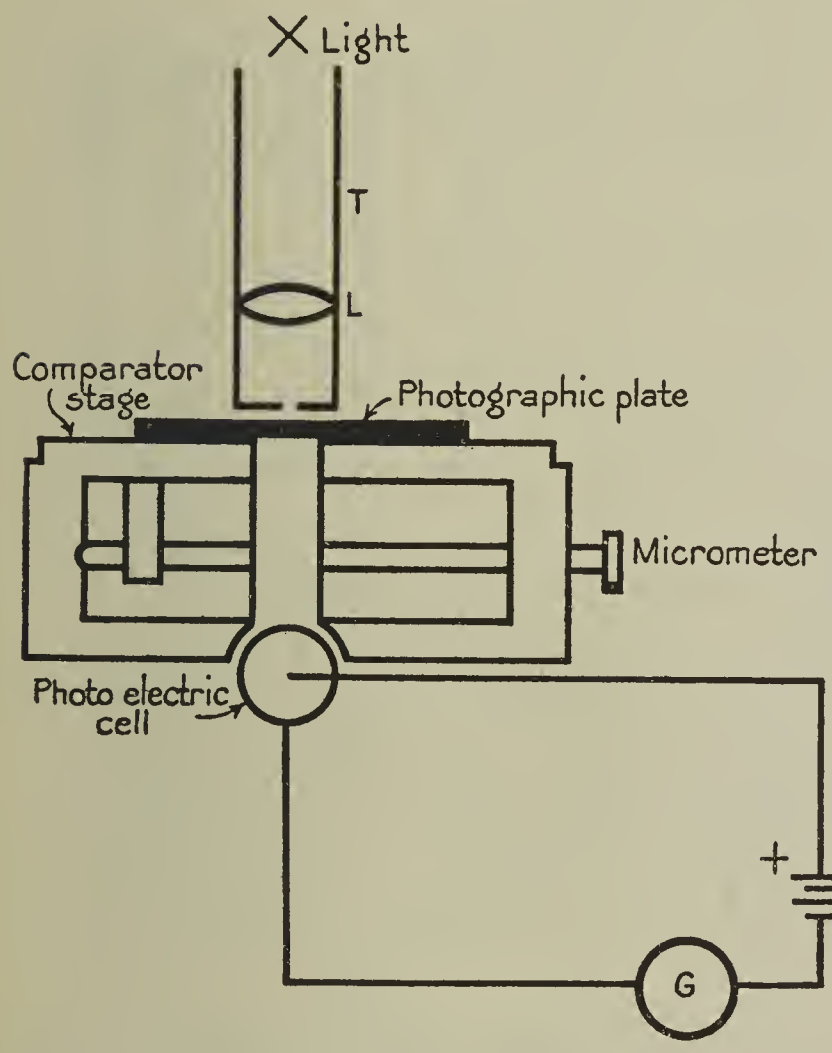


FIG. 27—The photo-electric comparator devised by Perrine

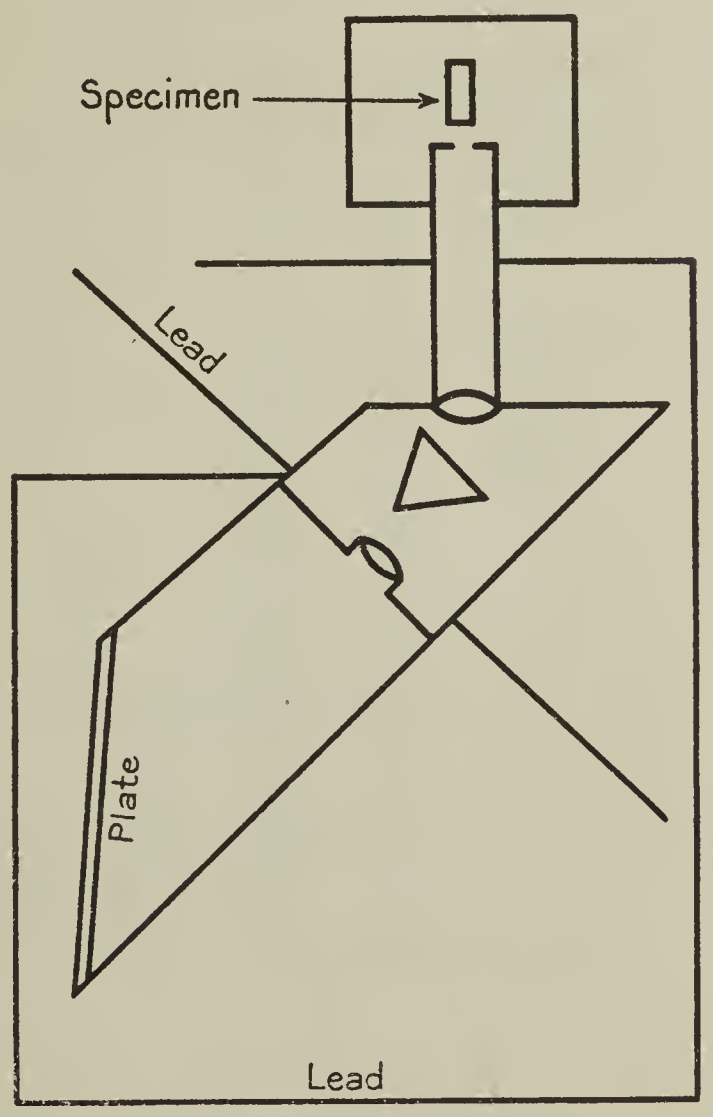


FIG. 28—The spectrograph

moved in a plane perpendicular to that of the figure and exposure could thus be made at various places on the same photographic plate. Stanley plates 6 cm. by 9 cm. were used. The intensity of fluorescent radiation was so small that an exposure of several hours was necessary, even though a slit-width of 0.15 mm. was used. As a source of X-rays a radiator-type Coolidge tube was used with a current of 2 to 3 milliamperes at 50,000 volts.

In taking photographs under the conditions described, it was found that diffusely scattered X-rays caused the plate to be badly fogged, even though the X-ray tube was provided with the usual lead-glass shell directly about the bulb. Protection from these scattered X-rays was secured by lead screens made of two layers of 1/16-inch thick

[1] J. O. Perrine. Phys. Rev. (2), XXII, p. 48, 1923.
[2] Zeitschrift für Instrumentenkunde, XXVIII, p. 34.

lead. In some plates a shadowgraph of a small metal clip on the near side of the plate-holder was obtained. This particular circumstance, together with the general fogging, indicated very definitely that diffuse X-radiation came from a brick wall about 3 feet away from the rear side of the spectrograph and the X-ray tube. It was found necessary to surround the spectrograph completely by these lead plates, and in the final arrangement satisfactorily clear negatives were obtained even after exposures of 15 hours.

FLUORESCENCE SPECTRA

The experimental results obtained by this method are given in tables XVIII and XIX, which contain lists of the numerous sub-

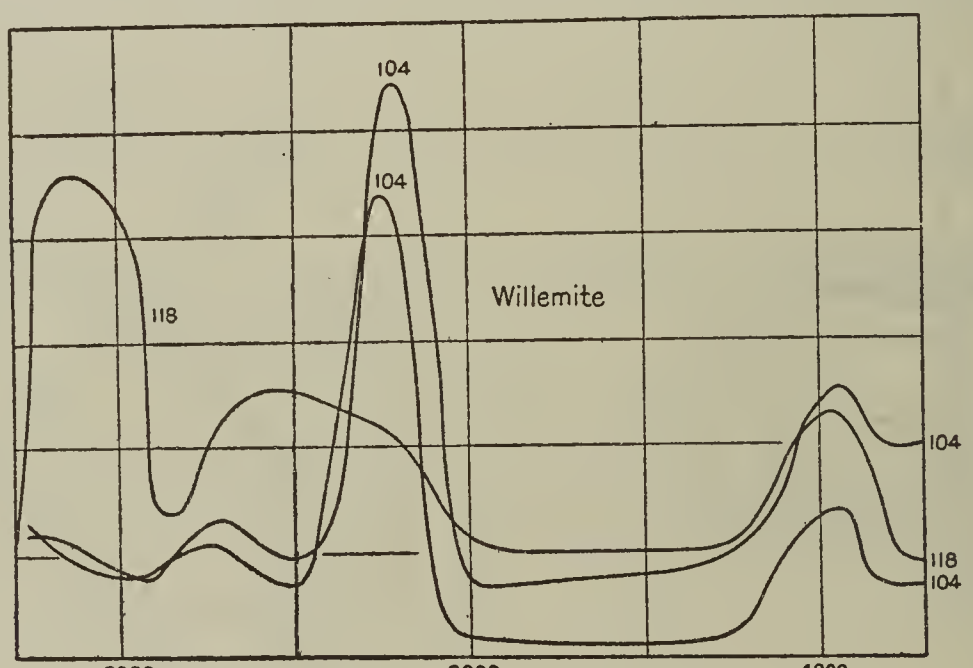


FIG. 29—Bands in the spectrum of willemite

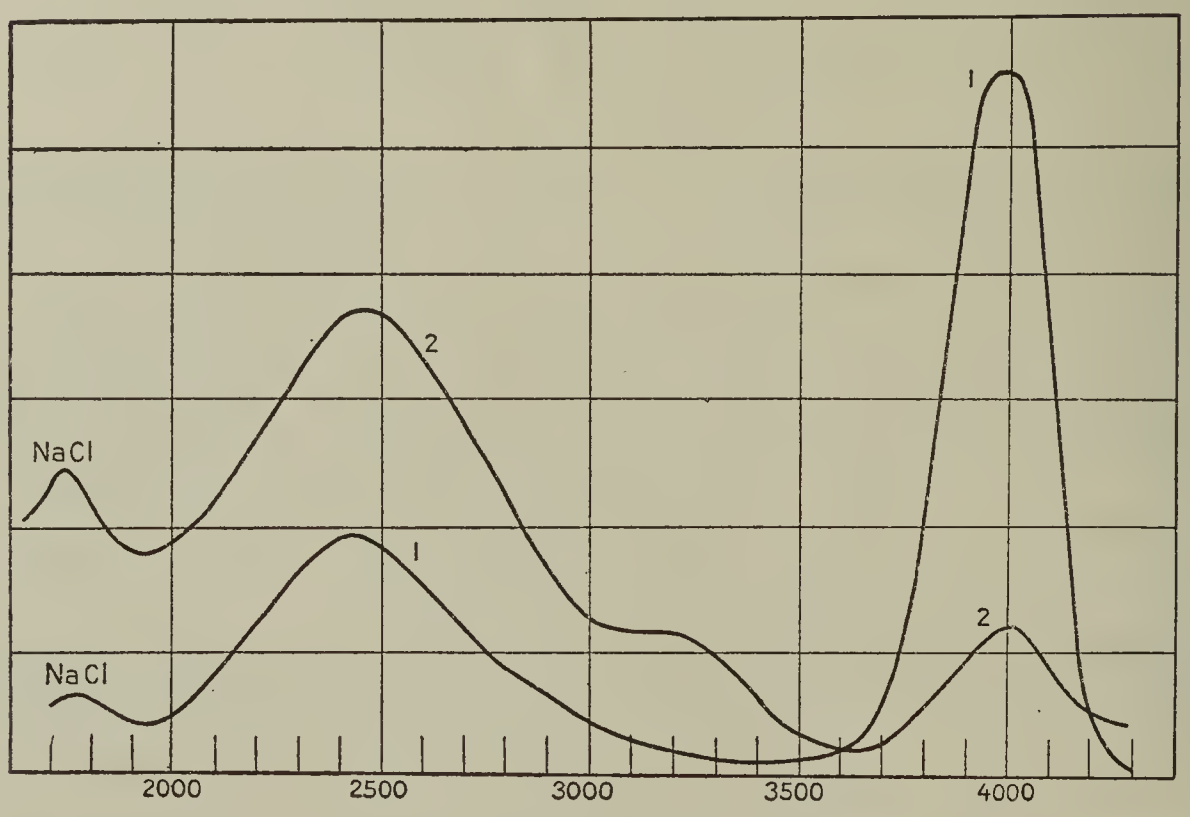


FIG. 30—Luminescence bands of NaCl

stances tested that showed fluorescence (table XVIII) or were inert (table XIX). The curves in figures 29 to 35 indicate the degree of

blackening of the negatives. Ordinates are galvanometer deflections, and since the *upper* left-hand corner of the diagram has been taken as the origin of axes, the maxima of the curves correspond to the region of greatest brightness.

TABLE XVIII—*Compounds which gave positive results*

Substance	Frequency number limits of band	Frequency number of maximum	Time of exposure to X-rays
Barium sulphate	2,000–3,700	2,610	6 hours
Barium sulphate / Radium sulphate	2,100–3,200	2,750	12 hours
Cadmium chloride	1,800–3,600	1,860, 2,250, 3,000	5 hours
Cadmium iodide	1,700–1,950	1,810	5 hours
	2,000–2,400	2,190	
Cæsium chloride	2,000–3,000	2,350	½ hour
	3,200–3,900	3,610	5 hours
	3,900–4,300	4,070	5 hours
Calcium tungstate	2,000–2,700	2,300	2 minutes
Cuprous iodide	2,100–2,450	2,300	10 hours
Lithium potassium chloride (Chem. Dept.)	2,800–2,880	2,840	12 hours
	2,880–3,600	3,220	
Lithium potassium chloride (50–50 mech. mixture)	2,000–2,600	2,220	4 hours
	3,000–3,600	3,220	
Lithium potassium chloride (50–50 recrystallized mixture)	1,800–2,600	2,300	10 hours
	2,600–3,600	3,200	
Lithium chloride	1,700–3,300	1,800, 2,300, 3,050	6 hours
Mercurous chloride	1,750–1,850	1,800	5 hours
Potassium chloride	2,050–3,400	2,250, 3,040, 3,140	8 hours
Potassium bromide	1,700–3,500	1,800, 2,200, 3,300	4 hours
Potassium iodide	1,700–3,500	1,800, 2,200, 3,000	14 hours
Rubidium chloride	1,800–3,500	1,870, 2,280, 3,280	12 hours
Sodium chloride	1,700–4,200	1,750, 2,450, 4,000	8 hours
Willemite Nos. 104 and 106	2,200–4,200	2,350, 2,770, 4,050	7 hours
Willemite No. 118	1,700–2,100	1,900	7.5 hours
	2,200–2,900	2,450, 2,700	
	3,800–4,200	4,040	
X-ray intensifying screen No. 3 (Patterson)	2,000–2,700	2,300	2 minutes
X-ray fluoroscopic screen No. 1 (Patterson)	1,600–2,780	Flat 1,800–2,320	5.5 hours
	1,700–1,900	1,810	
	1,900–2,600	2,190	
	1,800–2,500	2,210	
Zinc oxide	1,700–1,850	1,775	5 hours
	1,950–2,300	2,070	

TABLE XIX—*Compounds showing no ultra-violet fluorescence*

[The number following each salt indicates the number of hours exposure to X-rays. Salts marked with an asterisk give narrow fluorescence bands in the visible.]

URANYL COMPOUNDS

Ammonium potassium uranyl chloride (5)
*Barium uranyl acetate (12)
*Cæsium uranyl chloride (12)
*Cadmium uranyl acetate (8)
*Lead uranyl acetate (12)
*Lithium uranyl acetate (10)
*Mercuric uranyl nitrate (8)
*Potassium uranyl acetate (3)
*Rubidium uranyl nitrate (5)
*Rubidium uranyl sulphate (5)
*Silver uranyl nitrate (13)
Strontium uranyl acetate (2)
Thallous uranyl sulphate (8)
Uranyl tellurate (13)

OXIDES

Aluminum oxide (5)
Antimony oxide (12)
Barium oxide (10)
Bismuth oxide (10)
Berylium oxide (6)
Cadmium oxide (6)
Calcium oxide (12)
Calcium peroxide (5)
Cuprous oxide (5)
Cupric oxide (5)
Erbium oxide (10)
Germanium oxide (5)
Magnesium oxide (8)
Magnesium peroxide (5)
Silicon oxide (12)
Silicon dioxide (10)
Strontium oxide (6)
Strontium peroxide (5)
Tin oxide (12)
Uranium oxide (15)
Uranium peroxide (18)
*Zinc oxide (8)
Zinc peroxide (8)

MISCELLANEOUS COMPOUNDS

Anthracene (5)
Barium chloride (5)
Berylium chloride (7)
Cadmium bromide (5)
Cadmium fluoride (5)
Cadmium phosphate (5)[1]
Cadmium sulphide (5)[1]
Cæsium aluminum sulphate (5)
Cæsium di-chlor-iodide (5)
Calcium sulphide (10)
Chrysoidine (5)
Copper selenate
Cupric bromide (7)
Cupric sulphide (10)
Didymium chloride (7)
Eosin (crystal) (5)
Fluorescine (5)
Indium iodate (5)
Iron pyrites (5)[3]
Magnesium perborate (4)
Mercuric chloride (5)
Mercuric copper iodide (7)
Mercuric iodide (7)
Mercuric sulphide (5)
Molybdenic acid (5)
Molybdenite (6)[3]
Potassium auri bromide (5)
Potassium cuprisulphide (7)
Potassium fluoride (4)
Potassium fluotitanate (5)
Potassium periodate (7)
Rochelle salts (5)
Rubidium di-chlor-iodide (5)
Silver bromide (5)[2]
Silver chloride (5)[2]
Silver dichromate (5)
Silver iodide (5)[2]
Silver mercuric iodide (7)
Sodium boro-fluorate (5)
Sodium fluoride (5)
Sodium periodate (5)
Sodium silicate (5)
Stibnite (5)[3]
Strontium chloride (5)
Sulphur (block) (10)
Telluric acid (5)
Thallium bromide (5)
Thallium chloride (5)
Thorium nitrate (5)
Tin chloride (5)
Tungstic acid (5)
Zinc (sheet) (5)
Zinc bromide (4)
Zinc sulphide (12)[1]

[1] Reported by Dr. C. W. Waggoner as highly purified and not fluorescent under excitation by ultra-violet light.

[2] These three silver salts had been freshly prepared and kept from ordinary light at all times.

[3] These three sulphides were large crystals with flat mirrorlike surfaces.

All the curves in figures 29 to 35 have this in common: they show the presence in the visible and ultra-violet regions of the spectrum of two or more bands of fluorescence excited by X-rays and permit the location of the crests and roughly of the limits of these bands. These crests are undoubtedly group crests, since the conditions of measurement do not reveal the more intimate structure as in the determinations to be described in the subsequent parts of this chapter. If, however, we estimate as nearly as the diagrams permit the locations of the crests, averaging the readings for the various runs, we find that the distances between crests for each substance is an exact multiple of a constant-frequency interval, within the experimental errors, and that this frequency interval is in fair agreement with the Tanaka interval for the activating element of the salt. The results of such a computation are given in table XX.

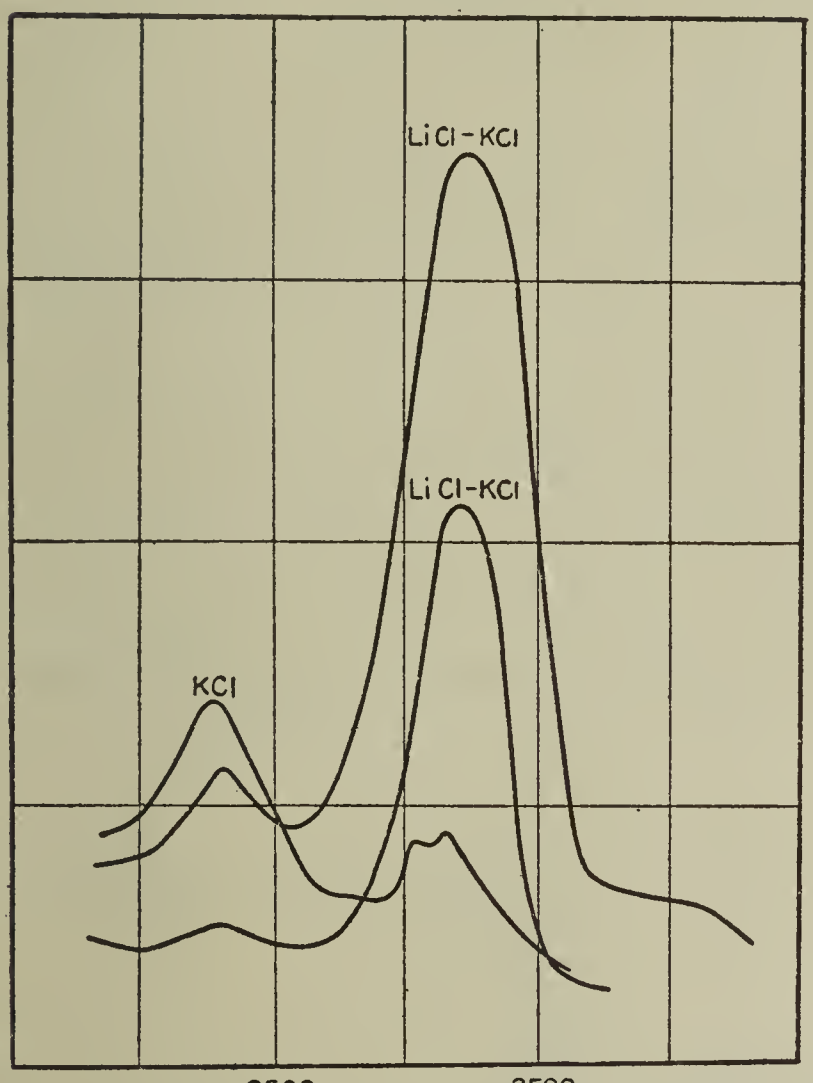


FIG. 31—Luminescence bands of KCl

TABLE XX—*Spectral structure of X-ray fluorescence*

Substance	$1/\mu \times 10^3$	Differences	Tanaka's interval	Remarks
NaCl (see fig. 30)	3,993 3,150 2,449 1,750	843 = 12×70.3 701 = 10×70.1 699 = 10×69.9 Av. 70.1	70.0	Average of two curves
KCl(1) (see fig. 32)	3,145 3,045 2,745(?) 2,245	100 = 2×50 300 = 6×50 500 = 10×50	Sets with 46.5 and with 51.2	From a single curve. The band 2745 is so flat crested that no value can be definitely assigned to the peak
KCl(2) (see fig. 33)	3,210 2,300	910 = 18×50.6	Do.	Average of two curves

TABLE XX—*Spectral structure of X-ray fluorescence*—Continued

Substance	$1/\mu \times 10^3$	Differences	Tanaka's interval	Remarks
KBr (see fig. 34) . . .	3,275 2,170 1,770	1,105=22×50.2 400= 8×50.0	Sets with 46.5 and with 51.2	From a single curve
KI (see fig. 34)	3,130 2,980 2,180 1,780	150= 3×50.0 800=16×50.0 400= 8×50.0	Do.	Do.
RbCl (see fig. 33) . .	3,275 2,274 1,872	1,001=40×25.0 402=16×25.1	25.6	Crest at 3275 very flat
$CdCl_2$ (see fig. 33) . .	3,010 2,245 1,862	765=38×20.1+ 383=19×20.2−	Sets with 18.7 and with 22.6	From a single curve
CsCl (see fig. 35) . .	4,072 3,610 2,368 1,848	462=23×20.1 1,242=62×20.0 520=26×20.0	From the curve, 20	Average of four curves
Willemite 104 *a* . . .	4,060 2,795 2,295	1,265=31×40.8 500=12×41.7	The activator is presumably Mn, for which Tanaka's best value is 42.0	From four runs taken separately
104 *b*	4,055 2,758 2,255	1,295=31×41.7 503=12×41.9		The general average of the interval is 40.9
106 *a*	4,002 2,782 2,378	1,220=30×40.7 404=10×40.4		
106 *b*	4,000 2,778 2,372	1,222=30×40.7 406=10×40.6		

The values of the wave-numbers ($1/\mu \times 10^3$) in table XX are not to be taken as more than rather roughly approximate. In one or two instances, in particular in the case of the value 2,745 in the list for KCl (1), where the crest is very flat, there is every reason to suppose the presence of two or more submerged components, one of which may reasonably be assumed to belong to the set given in the column of differences. It is therefore entered at the proper place with a question mark to indicate the uncertainty. While the data are by no means adequate for establishing the precise intervals, it is thought that they serve to indicate a *structure* in the ultra-violet fluorescence due to X-rays analogous to that known to prevail in photo- and cathodo-fluorescence in the visible spectrum, and also to show that in KCl, KBr, and KI the same interval occurs, *i. e.*, that proper to the activating element potassium.

A somewhat detailed scrutiny of these curves brings out several points of great interest.

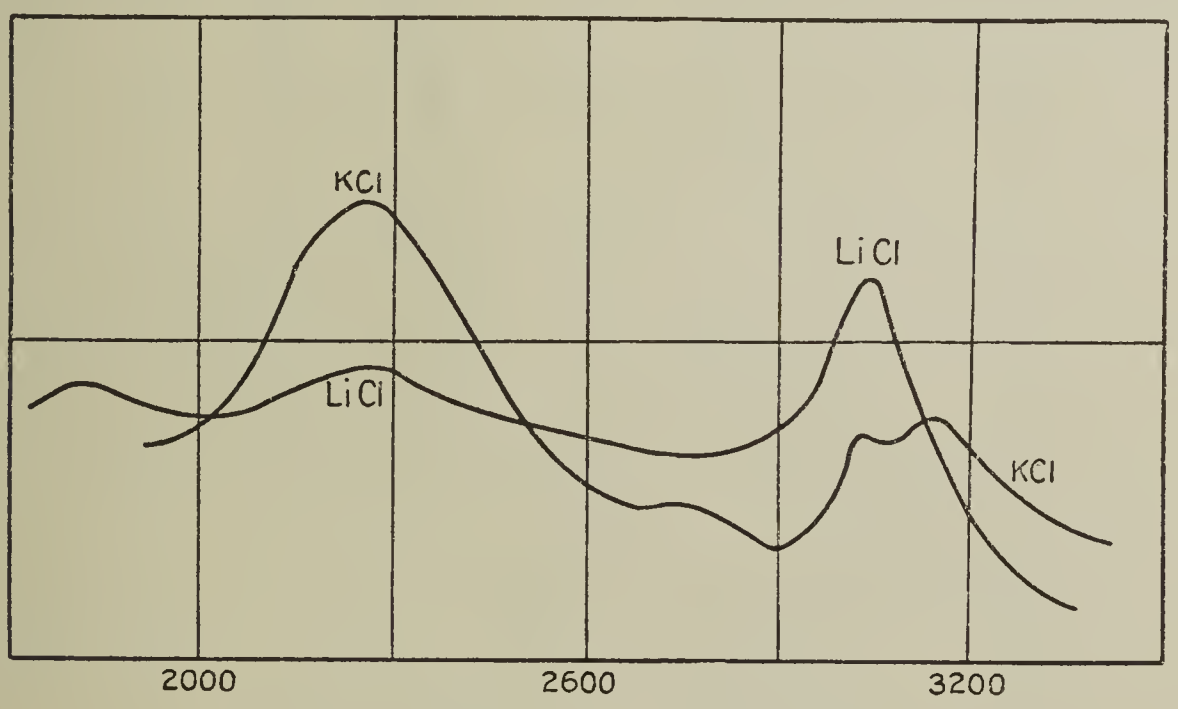


Fig. 32—KCl and LiCl compared

(1) Where repetitions are given as in NaCl (fig. 30), LiCl-KCl (fig. 32), CsCl (fig. 35), and willemite (fig. 29) it is apparent that while the location of the crests is in fairly good agreement for successive runs, there are very striking discrepancies in the relative brightness which can not be regarded as accidental. Since the ordinates represent the sum total of the luminescent output during the entire exposure, the brightness of the bands in the two samples can be compared only upon the assumption that the output per unit of time remains the same throughout the run, which we know is not the case. A sample of artificial willemite, designated by Perrine as No. 104, was prepared for these experiments by D. T. Wilber. It was subjected to two successive exposures of equal duration (7 hours) and equal intensity. The luminescent output, as measured by the

blackening of the plate, was materially greater in the first run, the ratios being shown in table XXI.

TABLE XXI—*Fatigue of willemite under exposure to X-rays*

μ	$1/\mu \times 10^3$	Blackening		Ratio
		Run 1	Run 2	
0.435	2,300	4	3.25	0.81
.357	2,800	16.4	13.2	.81
.247	4,050	7.7	4.2	.53

It will be seen from table XXI that the band in the far ultra-violet 0.247 is more fatigued by exposure than those of greater wave-length. Perrine excited this and other willemites again by X-rays after two or three months and found no signs of a *recovery* from the fatigue due to the previous exposures.

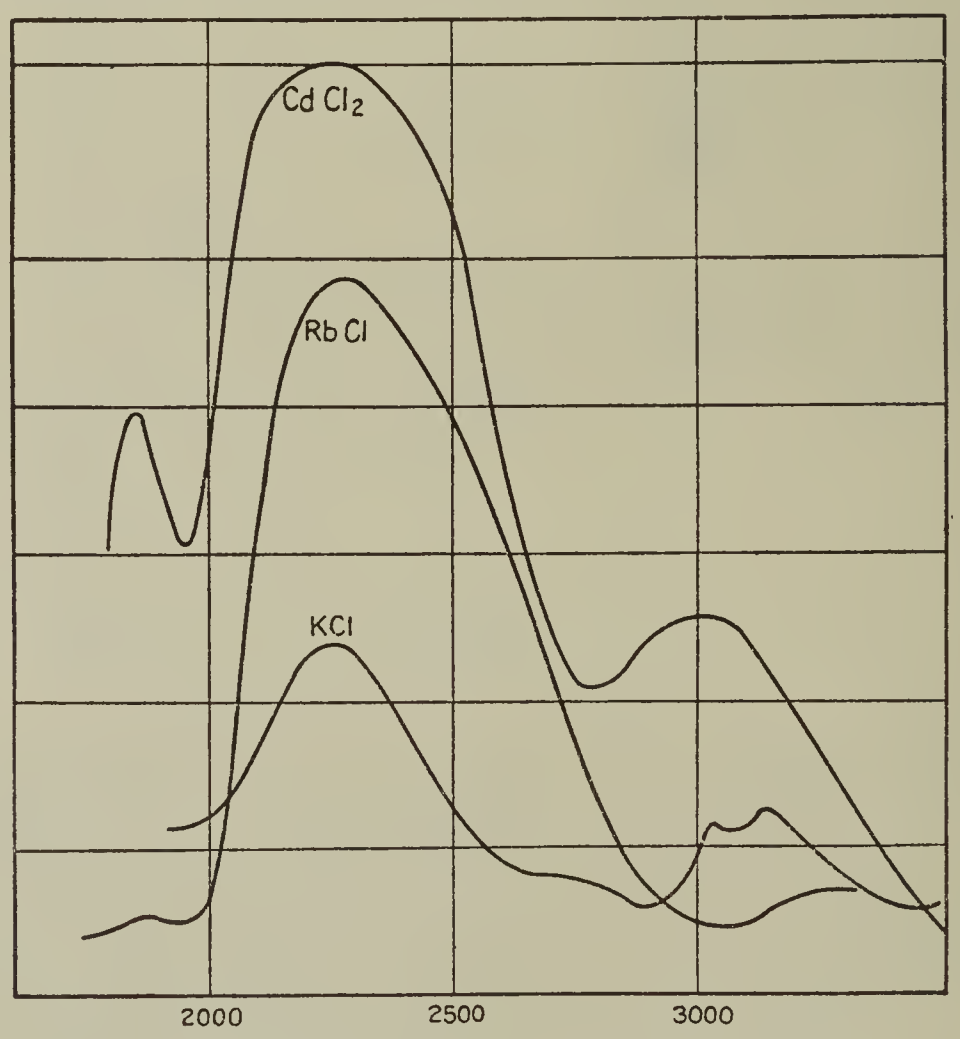


FIG. 33—Principal crests of KCl, RbCl, $CdCl_2$

(2) That striking differences as regards the width and location of bands may occur even in materials supposed to be practically identical in composition and mode of preparation is indicated in the curve marked 118 in figure 29. This applies to an artificial willemite, also prepared by Wilber. Whereas sample No. 104 showed only a trace of fluorescence in the green (0.526μ), which is the region of the bril-

liant glow in willemite excited by light or by cathode rays, and while the latter samples were also feeble in the region of the violet band (0.435μ), sample 118 has broad bands in the green and violet. The violet band overlaps both the violet and near ultra-violet, and the narrow band at 0.357μ is quite submerged. In the far ultra-violet, 118 and 104 are of the same order as to intensity and width. A similar divergence as to type is found in cæsium chloride (curve 4, fig. 35).

(3) Another divergence between substances supposed to be almost identical may be noted in figure 30, where two samples of sodium

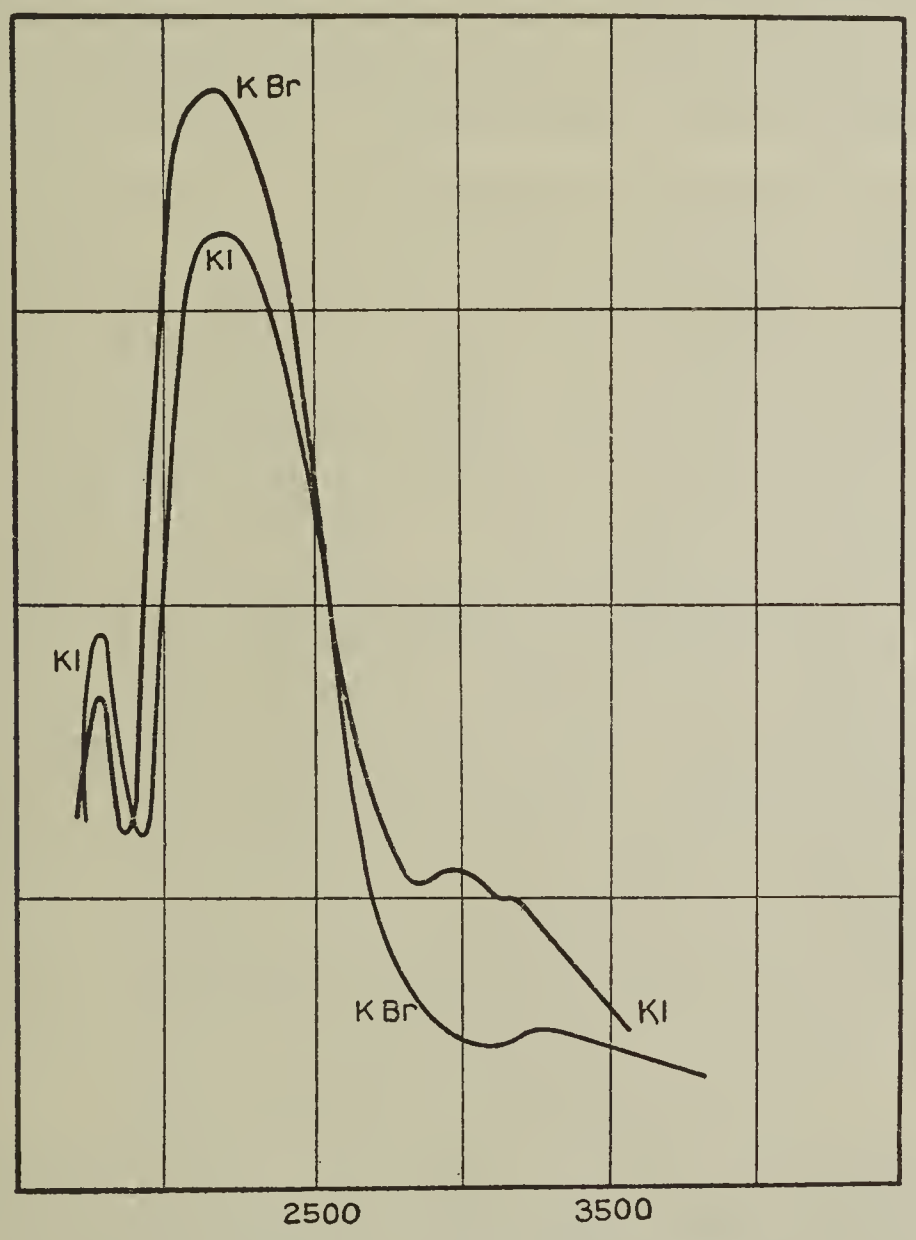


FIG. 34—Identity of bands of KI and KBr

chloride were exposed for 5 hours (curve 1) and 15 hours (curve 2) respectively. The enhancement of the band at 0.250μ (4,000), which might have been almost 14-fold instead of less than 5-fold had the exposures been equal, may be due to the fact that proportion of the activator was more nearly an optimum in sample 1. This view is strengthened by the measurements represented in figure 31, where two runs on a mixture of lithium chloride and potassium chloride are plotted. The crests of these curves correspond in location to those of the fluorescence bands of KCl shown in the same diagram for comparison, but the ultra-violet band is greatly enhanced in the curves

for the mixture. That the activator here is potassium and not lithium is indicated by the frequency-interval [see table XX, KCl (2)]. A measurement of lithium chloride (fig. 32) gave a curve the crests of which are those of KCl, both as to interval and location, with the ultra-violet band somewhat enhanced, from which we infer that a trace of KCl was probably dominant and suppressed whatever fluorescence due to lithium might otherwise have appeared. Similar cases are known in cathodo- and photo-luminescence. (See section II of Chapter VI of this treatise.)

The curves in figure 33 ($CdCl_2$, RbCl, KCl) and in figure 34 (KBr and KI) are of interest, aside from the determination of the frequency intervals, as showing the approximate coincidence of the positions of

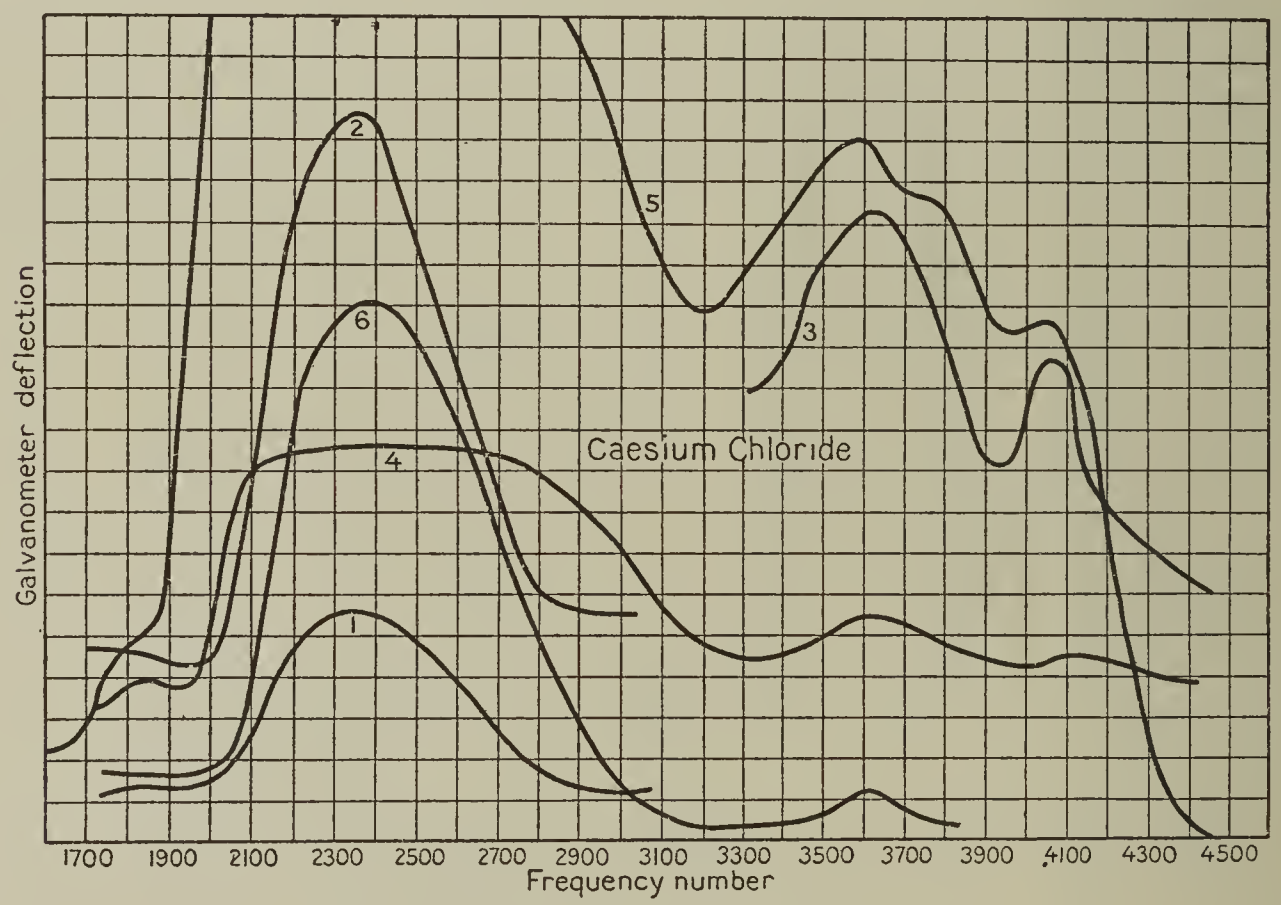


Fig. 35—Bands in the spectrum of CsCl

the principal crests of allied compounds. To facilitate comparison, these and similar crests from the foregoing figures are sketched together in figure 36. No such simple relationships between molecular weight and wave-length of crests as that described by Tanaka (see Chapter III) is here apparent.

II. COLORATION BY X-RAYS

(Describing experiments by P. L. Bayley.)

In the course of his experiments, Perrine noticed certain marked color changes of the sort first described by Holzknecht.[1] He remarks:[2]

"Highly purified rubidium chloride, which is a white salt, became a dark blue, looking much like a piece of copper sulphate. This color-change was observed after an exposure of five hours. The photographic plate gave evi-

[1] Holzknecht. Verh. Deutsch. Phys. Ges., IV, 25, 1902. [2] Perrine, l. c.

dence of both visible and ultra-violet fluorescence. It was then a question whether or not this specimen, already a dark blue, would fluoresce upon further excitation by X-rays. It was found to fluoresce as strongly as before. Upon removing the specimen and exposing it to ordinary daylight, the original whiteness returned within three hours.

"A sample of highly purified sodium chloride turned to a marked buff color. The original whiteness of the salt was not restored in three days. Potassium chloride and lithium chloride became pink under the action of X-rays. In these two cases the original color returned within an hour. Potassium bromide took on a light blue and potassium iodide a brown-buff color. Cæsium chloride turned to a dark blue and returned within an hour.

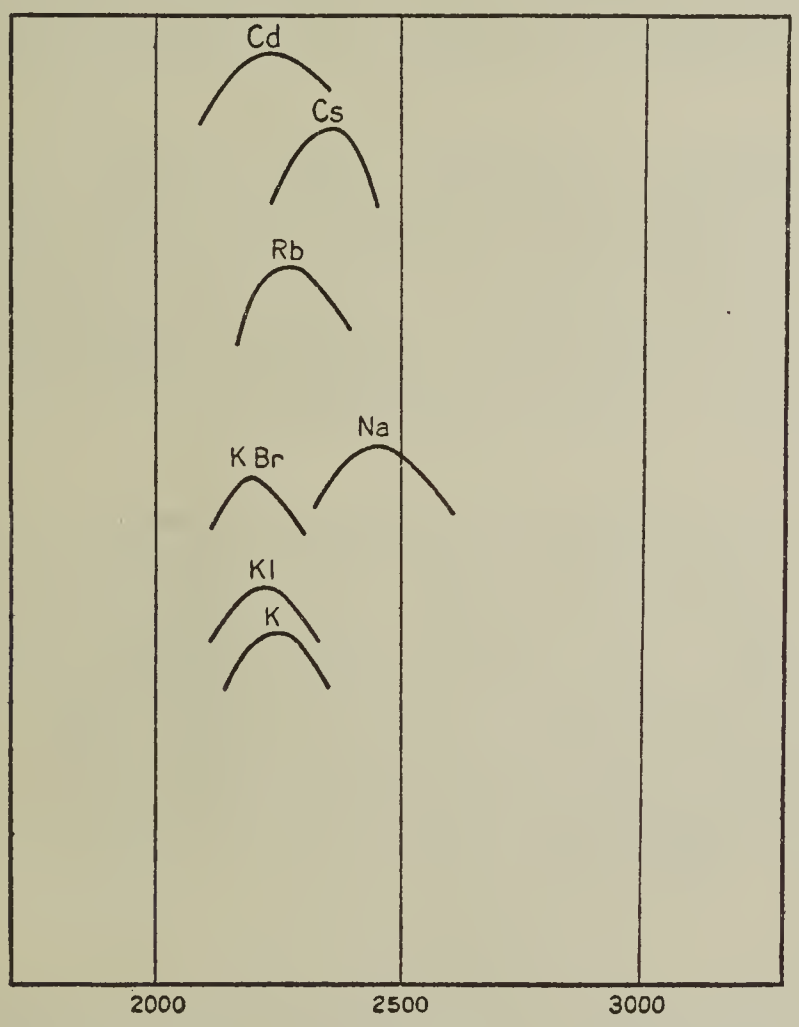


FIG. 36—Principal crests compared as to frequency

As in the case of rubidium chloride, cæsium chloride, which had been turned blue by exposure to X-rays, was tested again and fluoresced equally well during the second exposure. To determine whether there might be some fluorescent radiation emitted during the time in which the original white color was returning, the substance was left in the light-tight box, the photographic plate moved to a different exposure surface, and a 36-hour exposure taken. At the end of this time, the specimen was still as blue as at the beginning and no evidence of fluorescence appeared on the plate. It was found on exposure to daylight that the substance turned white within five minutes.

"It is not unlikely that these color changes were due to a reduction of a small fraction of the chloride into the metal concerned and free chlorine. The chlorine, perhaps, is retained by absorption in the unreduced portions. The entire mass appeared to be changed in color, but it is very possible that the reduction of a small amount is sufficient to give color to the entire mass. Exposure to light appears to be necessary in order to reverse the change. The fact that a specimen exposed once gave further fluorescence on a second

exposure would not necessarily indicate that the fluorescence did not accompany the color change. As stated above, a small amount of reduced salt might color the entire mass so that during the exposure the continual reduction might occur with resulting fluorescence. To the eye, however, no additional color changes took place.

"Whenever the specimen, after an exposure, showed a color change the developed plate gave evidence of ultra-violet fluorescence, except for silver bromide, silver iodide, and silver chloride. The color changes in these three salts were much less than had been expected, since they show marked color changes when exposed to ordinary daylight.

"The rubidium, potassium, and sodium chlorides had been carefully prepared and were highly purified as far as the presence of other metals was concerned. Spectroscopic examination confirmed the absence of calcium and magnesium."

Subsequently Dr. P. L. Bayley[1] made a more extended study of this effect. After observing the lines produced in many compounds by exposure to X-rays he studied in detail the colors of halite (natural sodium chloride) and of sylvite (natural potassium chloride). The following description of this investigation is from his paper in the *Physical Review:*

"A Coolidge X-ray tube of 30 milliamperes capacity was used and was operated at 50 kv. and 3 milliamperes. The samples were placed in a thin light-tight paper box within two inches of the tube and not more than five inches from the target. In all cases reported, where no color developed, the exposure was of five hours duration. The radiation was sufficiently strong to produce noticeable coloration in CsCl and KCl within five minutes. A fan was kept running to keep air circulating around the X-ray tube so that the samples would not get warm from the heat from the tube, since heating as well as exposing to light fades these colors.

Study of Hues

"The hue produced depends upon the preparation of the sample. The coloration due to an impurity may mask that of the chemical under study,[2] and moisture of the sample may prevent coloration.[3] The more highly divided the particles of the material, the more unsaturated[4] are the colors. This is due to the large amount of white light reflected from the innumerable faces of the crystals of the powder. Although meaningless in general, the saturation of a few colors is given below in order to show a markedly higher saturation for those materials than for others of the same crystal size. In all the following work concerning the hues, the material was prepared in a fused mass or in as large crystals as possible, so that coloration could be most surely detected if it existed.

"In the table below [Table XXII] are shown the hues observed for a group of halides. The results of a few other experimenters are included in order to show the variation in the colors obtained. The small letters after the

[1] Bayley. Physical review (2), XXIV, p. 495, 1924.
[2] Goldstein. Nature, 94, 494 (1914).
[3] *Ibid.* Ann. der Phys., 54, 371 (1885).
[4] Doelter. (*a*) Das Radium und die Farben, Dresden (1910), contains references to all important papers of the subject up to the date of publication; (*b*) Sitz. d. K. Akad. Wiss. Wien (I), 121, 891 (1912); (*c*) *Ibid.* (II), 119, 1091 (1910).

hue indicate the speed of fading of the sample exposed to the daylight of an ordinarily light room; the capital letter refers to the experimenter, when other than the author, and the final small letters to the methods of preparation of the samples, all as shown in the key following the table.

"Since there seems to be no correlation between the color and the position of the element in the chemical table, no attempt has been made to state the exact hues. The word "bright" refers to the brilliance and "deep" means highly saturated.

"The chlorides of cæsium, rubidium, and potassium were of such exceptional purity that the highly saturated colors produced in them, if due to impurities, must be due to extremely minute traces. Furthermore, since the same hues are obtained in materials prepared by widely different methods, the coloration must be caused by the same impurities left in the compounds by several of the usual methods of purification.

"The following materials also were found to be colored by X-rays: AgCl, permanent bluish gray; $BaCl_2+2H_2O$ and $BaCl_2$, pale yellow; $BeCl_2$, trace of yellowish brown; $CaCl_2$, pale yellow; CaF_2, natural crystal, purplish gray; CdI, permanent brown; HgCl, permanent brown; and K_2SiO_3 fused in flame, grayish blue.

TABLE XXII—*Coloration of alkali halides by X-rays*

[For comparison coloration due to cathode rays is given in round brackets, and coloration by radium rays in square brackets]

Fluoride	Chloride	Bromide	Iodide
Cs. Greenish blue, *bce*.	Deep blue, *f*, *abd*. . . .	Blue, *vf*, *ab*.	. . . . .
	(No color—G).	. . . . .	. . . . .
	[Greenish—D].	. . . . .	. . . . .
Rb. Purple, *h*, *bce*.	Deep sky blue, *m*, *ad*	Greenish blue, *vf*, *be*	No color, *be*
	(No color—G).	. . . . .	(Yellowish—G)
K. No color, *bce*.	Deep purple, *f*, *abd*. .	Blue, *m*, *b*.	Green, *m*, *b*
	Violet, *f*—H.	(Blue green, *m*—H). .	
	(Blue, *f*—N).	[Sea green, *f*—N]. . . .	[Brown—N]
	(Violet—G).	(Deep blue—G).	(Bright green—G)
Na. No color, *ac* (rose—G)	Amber, *d*, *ab*.	No color, *a*.	Brownish yellow, *d*, *b*
	Chamois yellow, *m*—H	. . . . .	. . . . .
	[Trace yellow—D]. . .	. . . . .	. . . . .
	([Brown—N]).	. . . . .	. . . . .
	(Amber, *m*—G).	(Rose lilac—G).	(Heliotrope, *m*—G)
Li. No color, *bce*.	Faint yellow, *h*, *b*. . . .	. . . . .	. . . . .
	Straw, *d*, *c*.	. . . . .	. . . . .
	(Purple—G).	(Dark gray—G).	(Brown yellow—G)

Preparation of materials (when not otherwise stated, the material was only c. p. grade):

a. Open to atmospheric moisture.

b. Heated to about 200° C. in a Pyrex tube; at that temperature the tube was sealed off with a flame some distance from the end of the tube so that moisture from the flame could not reach the sample.

c. Fused as a bead on a platinum wire in a Bunsen flame; bead placed in a Pyrex tube and treated as in *b*.

d. Prepared by Dr. J. Papish of the chemistry department, exceptionally pure; contained only spectroscopic traces of sodium, calcium, magnesium, iron, and silicon.

e. Prepared in physics department by D. T. Wilber; made in paraffined-paper dishes from c. p. halogen acid and alkali carbonate which was especially free from other alkalis.

Time of fading

vf. Very fast, 1 minute or less
f. 1 to 5 minutes
m. 5 to 30 minutes
h. 30 minutes to several hours
d. One or more days

Experimenter

D. Doelter[1]
G. Goldstein[2]
H. Holzknect[3]
N. Newberry and Lupton[4]

[1] Op. cit.

[2] Goldstein, Nature, 94, 494 (1914) and other references. See also Doelter's work just cited.

[3] Holzknect, Verh. Deutsch. Phys. Ges, 4, 25 (1902).

[4] Newberry and Lupton, Manchester Mem. 62 (1918).

"The following showed no coloration with 5 hours exposure: $AgNO_3$, Ag_2SO_4, $CsCl_2I$, $CsClBrI$, $CsAl(SO_4)_2+12H_2O$, $Cs(NH_4)Cl_2$, $Ca(CH_3CO_2)_2$, KCH_3CO_2, $KHCO_3$, KNO_3, K_2SO_4, K_2SiO_3 (powdered), Li_2CO_3, Na_2CO_3, $NaNO_2$, Na_2MoO_4, Na_3AlF_4 (cryolite), Na_2SO_4, NH_4Cl, $(NH_4)_2SO_4$, $ZnCl_2$.

Spectral Absorption of Halite and Sylvite Colored by X-rays

"The sample of halite, which was quite clear, was a gift from the International Salt Co. of New York, Ithaca, N. Y., and came from the Detroit Rock Salt Co. A thin slab about 1 cm thick was cut out along natural cleavage planes. It was then ground down on very fine sandpaper until the thickness was uniform as tested by a micrometer caliper. The surfaces were polished by rubbing on chamois skin, one-half of which was barely moistened with water. While the sample was being rubbed back and forth on the moist portion, it was gradually drawn toward the dry portion, the rubbing being stopped just as the surface became dry. This process gave fairly polished surfaces.

"The transmission was measured in the visible spectrum with a Schmidt and Hensch spectrophotometer. The transmission in the ultra-violet out to 0.200μ was measured by Miss S. A. McNulty with a Hilger sector disk spectrophotometer as modified by Howe,[1] and in the infra-red to 2.5μ by Prof. J. R. Collins.[2] The original sample showed a transmission of 0.87 at 2.5μ, which decreased rather uniformly to 0.20 at 0.200μ. After coloration the sample showed absorption above that of the uncolored sample in the region between 0.3μ and 1.3μ. The curve plotted with ordinates equal to the ordinates of the transmission curve of the uncolored material minus those of the colored material will be referred to as the *color transmission* curve of the material. In the same terminology, then, the color absorption of halite begins at 0.3μ, has its maximum at 0.46μ, and ends at 1.3μ. The color absorption band is fairly pronounced, the ordinates of half the maximum occurring at 0.4μ and 0.5μ. The sample was left exposed to daylight during all of the following week and its transmission measured every day. The yellow color grew more faint, but at every test the maximum absorption was found at 0.46μ.

"Many samples of rock salt from Detroit and Louisiana were colored and then heated quickly over a Bunsen flame. The color faded rapidly, but in no case did a blue color develop as has been reported for the case of coloration by cathode-ray bombardment.[3] In a few samples a very pale pink color seemed to remain after the yellow vanished, but in every case all color disappeared when the heating was continued to the point of the explosion of the crystal.

"The sample of sylvite from Stassfurt was obtained from the Ward Natural Science Establishment. A plate about 2 mm. thick was prepared in the same manner as that of halite. The sample faded so rapidly, as a result of the light passing through it when its transmission was being measured, that in ten minutes all color had disappeared. The transmission was determined at intervals of 0.04μ from 0.47μ to 0.67μ. Settings of the Schmidt and Hensch instrument were made as rapidly and at as regular intervals as possible back and forth throughout the range. Thus a non-repeating set of curves was obtained showing less and less absorption, but each curve showed a maximum absorption at 0.55μ with half values at about 0.48μ and 0.63μ.

[1] H. E. Howe. Phys. Rev. 8, 674, 1916.
[2] J. R. Collins. Phys. Rev. 20, 486, 1922.
[3] Goldstein. Sitz. d. K. Akad. d. Wiss. Berlin, 1894, p. 937.

Rate of Fading of Colors

"The blue produced in cæsium bromide by X-rays fades in less than 10 seconds exposure to daylight and is the shortest lived of any color observed by the author. The amber color of rock salt is the longest lived. Sylvite fades rapidly enough to enable its rate of fading to be quickly determined. The same sample of sylvite used above was colored to 0.44 transmission. The spectrophotometer was set at 0.55μ, the position of maximum absorption. The adjustable slit was adjusted continuously to keep the fields matched in intensity and at regular intervals of time the slit-width was recorded. The sample was again colored to 0.30 transmission, as it happened, and its rate of fading observed. A third test from 0.33 transmission was made. The data are shown in figure 37. The curves have been shifted along the time

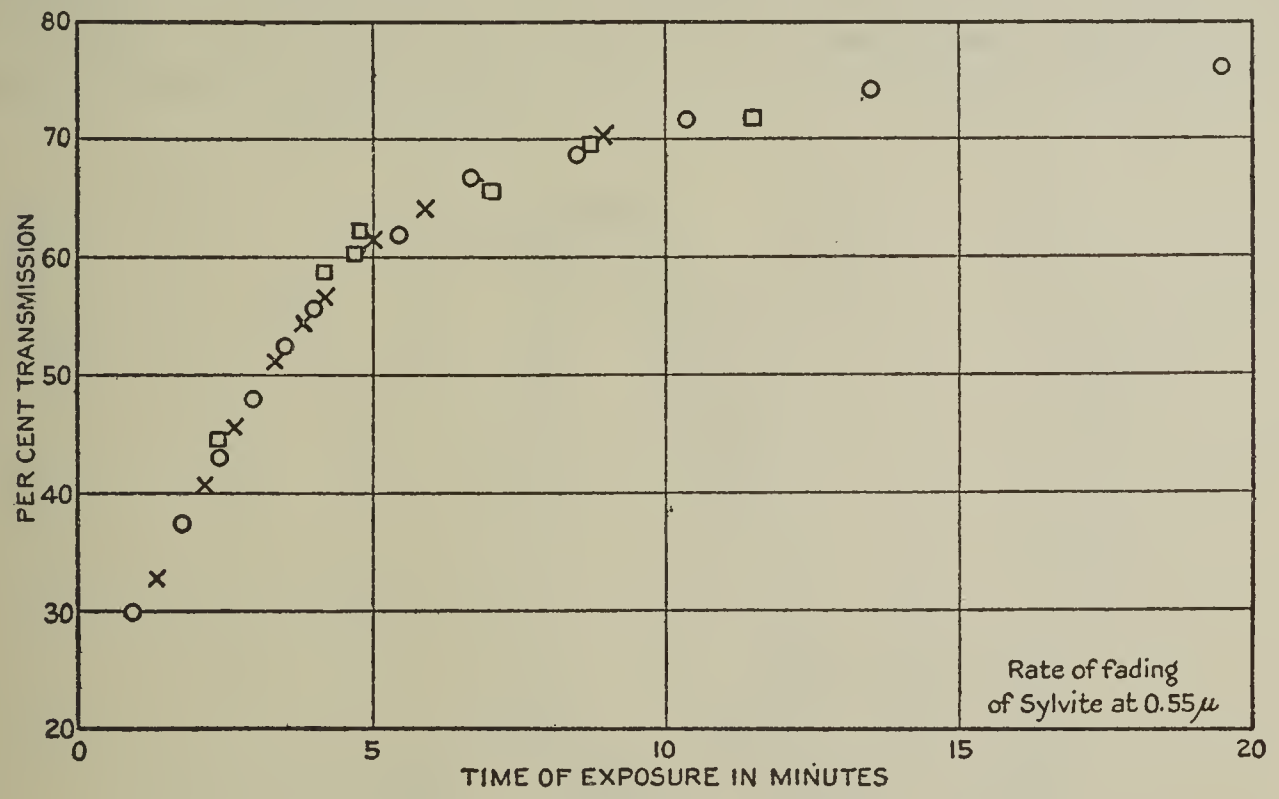


Fig. 37—Rate of fading of sylvite on exposure to daylight after coloration by X-rays (Bayley)

axis to make the initial values of each curve coincide. It is seen that alternate coloration and fading do not change the optical transmission of the material. The curves vary slightly but not consistently. The rate of fading is approximately proportional to the existing saturation of the color, which suggests that the recombination involved is an ordinary photochemical reaction.

Spectral Fading of NaCl, KCl, RbCl, and CsCl

"These four chlorides show highly saturated colors. They were each ground to a fine powder in a glass mortar and pressed in a very thin uniform layer on a glass plate. They were then moistened with a saturated solution of their respective salts and left to dry. Lithium chloride is too hygroscopic to be studied by this method. The materials formed a smooth surface sticking tightly to the plate, practically a thin sheet of very tightly packed crystals which had a minimum amount of reflected white light and so showed decided colors after exposure to X-rays. A plate of one of the colored salts was put in a plate-holder and placed in a spectrograph. The image of a type C 500-watt mazda lamp with filaments in a plane was formed on the slit of the spectroscope. After a short exposure the plate-holder was removed and the sample examined in a very dim light. The edges of the region of the material that was faded white were marked with a fine pencil

and the material given a further exposure and the whole process repeated. Except for NaCl the edges of the faded region could be determined within 1 mm or 0.01μ. The total exposures were approximately 10 sec., 30 sec., 1 min., 5 min., and 10 min., but for NaCl the exposures made with wide slits were several hours and the edges of the faded regions were very indefinite. The results are shown in figure 38. The scales of the time ordinates have been changed for each curve to make them fit into the same space. After about 50 times the exposure necessary to produce the first noticeable fading, further exposures produced only extremely slow widening of the faded region.

"The points of tangency of the curves with the wave-length axis give the wave-length of most rapid fading. The maxima for NaCl and KCl are shifted toward the long wave-length side of the maximum absorption of halite and sylvite respectively. To show that the shift was caused by the larger amount of energy in the red end of the spectrum from the mazda

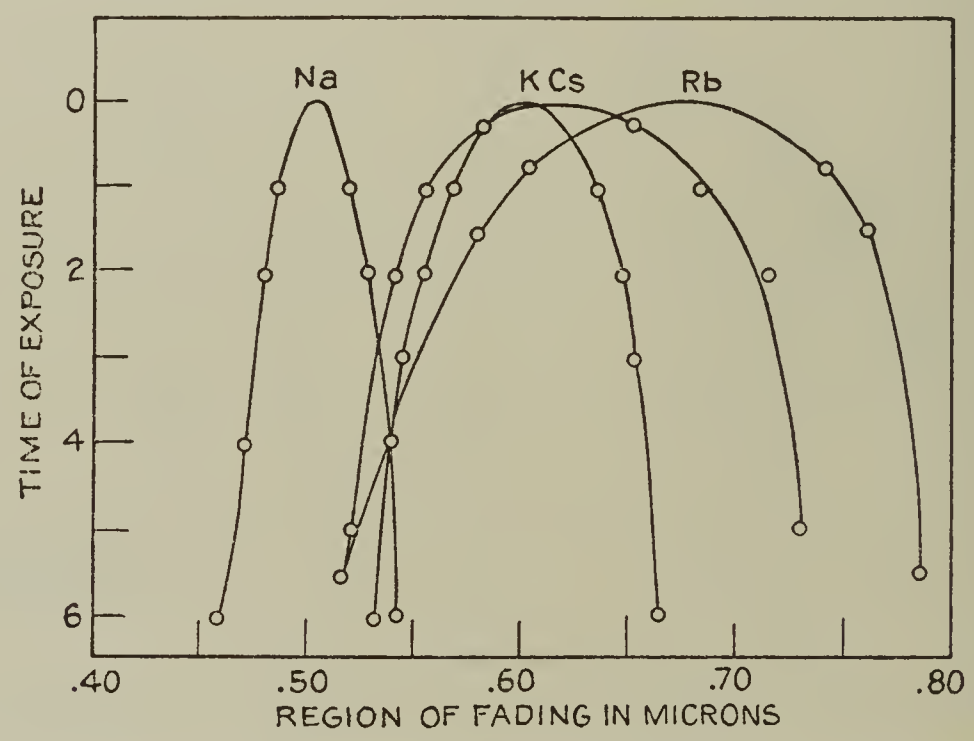


FIG., 38—Limits of faded region as a function of time of exposure in the spectrograph, in arbitrary units (Bayley)

lamp, the energy distribution from the lamp operated at 2850°C was calculated from Planck's radiation formula and corrections made for the absorption of the crown-glass prism. A curve was plotted with the ordinates given by the product of the energy incident upon the sample and the per cent color absorption of the sample. Those ordinates then represented the relative amounts of energy actually absorbed by the material and it was found that for halite and sylvite such curves had maxima respectively at 0.50μ and 0.595μ, which are close to the wave-lengths of most rapid fading. The positions of the regions of most rapid fading are not all in the order of the atomic number of the alkali metals. That may be due to a peculiarity in the color absorption of RbCl and CsCl. Since large enough crystals of the latter two chlorides can not be obtained to make their color transmission determinable, it is hoped that their absorption can later be measured by the light which they reflect, although their rapid fading will make the work difficult. From the two cases completely studied it seems quite probable that the fading of materials colored by X-rays is primarily due to the energy gained by their color absorption alone."

III. ULTRA-VIOLET FLUORESCENCE BY MEANS OF CATHODE RAYS

[Studies of photographs by P. A. Northrop.]

Shortly after the completion of the work of Dr. Perrine, an exploration was made by P. A. Northrop[1] of ultra-violet fluorescence where excitation was by cathode bombardment instead of X-rays. Each

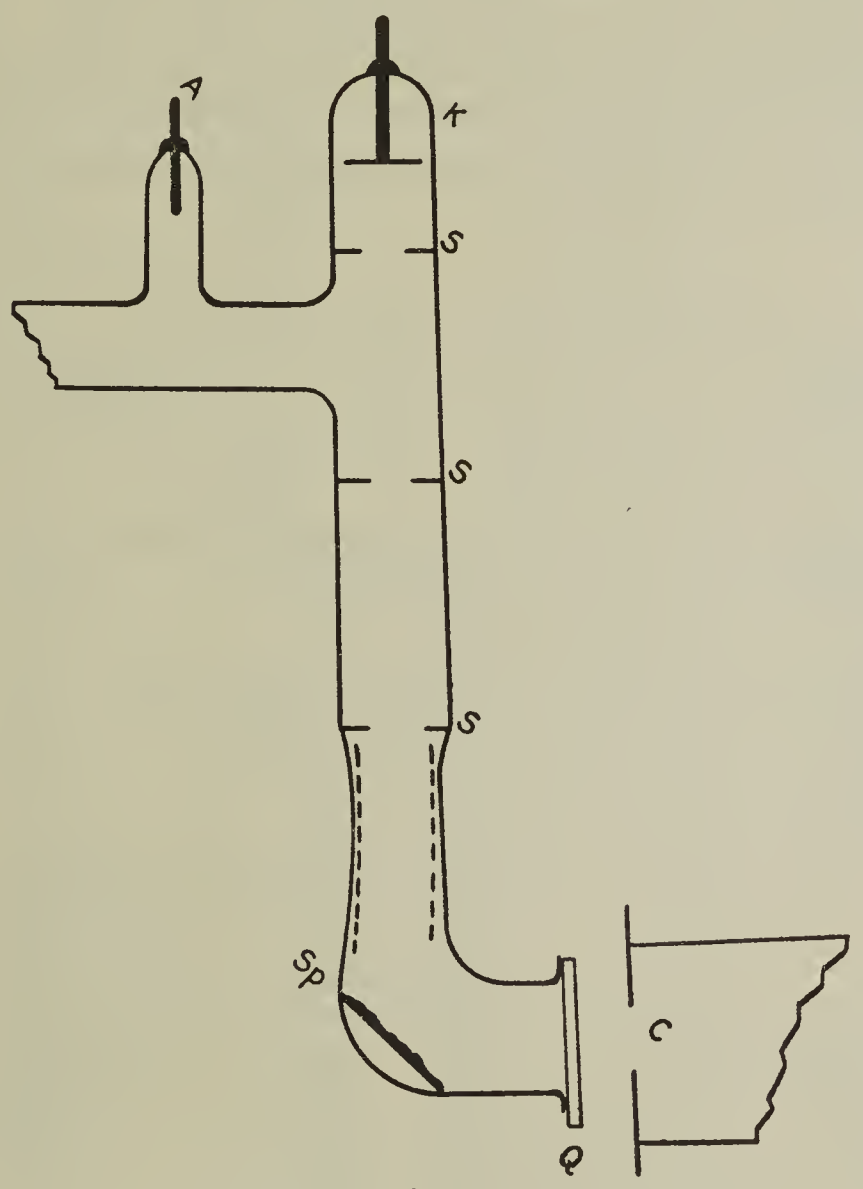


FIG. 39—Vacuum-tube for photographing cathodo-luminescence (Northrop)

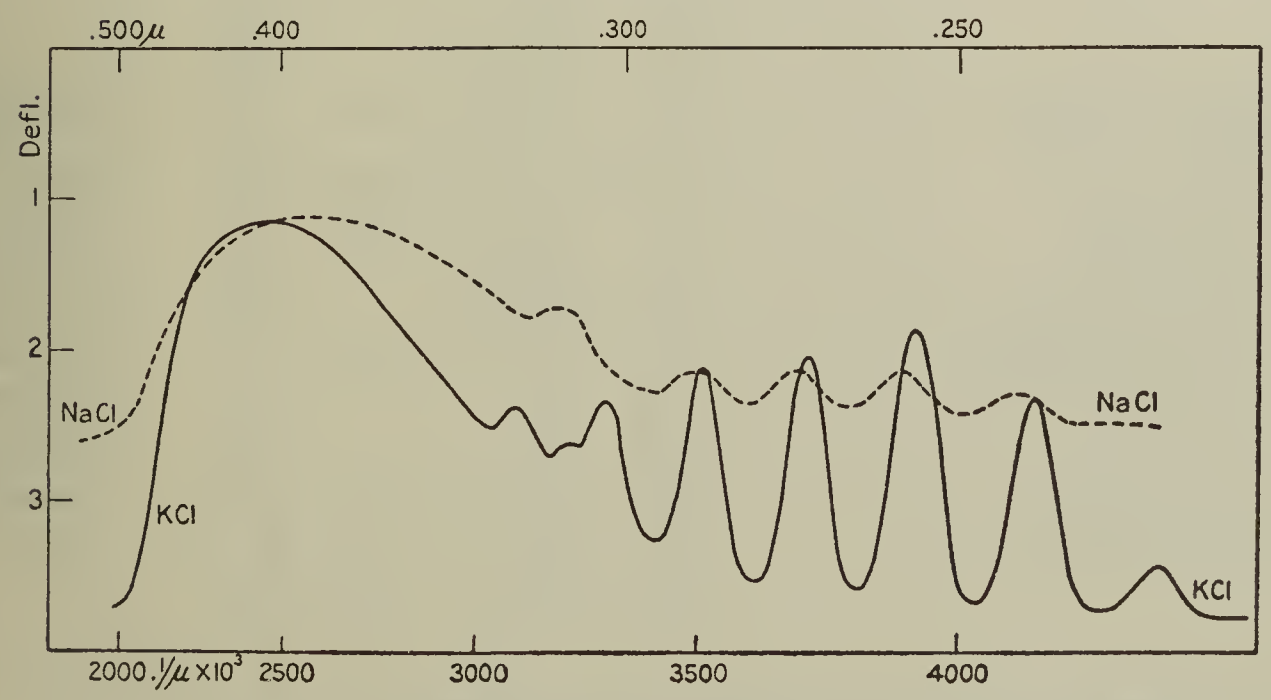


FIG. 40—Bands in the ultra-violet fluorescence spectrum (Northrup)

[1] P. A. Northrop. Thesis in the library of Cornell University, 1926.

of the specimens to be examined was placed in a tube of the form shown in figure 39, where *Sp* is the substance under bombardment, *K* the cathode, *A* the anode, and *Q* a quartz window. *S, S, S,* are metal diaphragms and *Al* a cylinder having the purpose of further shielding the walls of the tube from the cathode rays. The discharge through the tube was from a suitable induction coil. The collimator (*C*) of a small Fuess spectrograph with optical system of quartz was directed toward the specimen under bombardment, as shown in the figure. The list of substances photographed is given in the following tables:

TABLE XXIII—*Substances giving spectra.*[1]

Substance	Band limits (μ)	Band maximum. (F=Flat)	Exposure
CHLORIDES:			
Barium chloride	0.528–0.232	F 0.444–0.351	6 minutes
Berylium chloride	.499– .251	.372	3 hours
Cadmium chloride	.502– .347	.451	7 hours
	.347– .294	.326	
Cæsium chloride	.523– .316	F .437– .384	1 hour
	.316– .216	.274	
Lithium chloride	.502– .372	.450	2 minutes
	.372– .266	.342	
Potassium chloride	.513– .329	.402	(?)
	.329– .313	.323	
	.313– .294	.303	
	.294– .278	.285	
	.278– .263	.269	
	.263– .249	.255	
	.249– .236	.242	
	.236– .226	.230	
Rubidium chloride	.528– .297	.435 (?)[2]	4 hours
	.297– .216	.286 (?)[2]	
Sodium chloride	.507– .294	.387	1 hour
	.294– .279	.288	
	.279– .264	.271	
	.264– .250	.258	
	.250– .239	.245	
	.239– .232	.235 v.d.	
Strontium chloride	.528– .281	F .415– .377	1 minute
OXIDES:			
Aluminum oxide	0.528–0.223	F 0.426–0.384	5 hours
Barium oxide	.528– .274	F .444– .380	5 hours
Berylium oxide	.528– .202	F .319– .244	15 minutes
Calcium oxide	.522– .274	.375	6 hours
Magnesium oxide No. 1	.523– .300	.405	(?)
Magnesium oxide No. 2	.528– .319	F .397– .351	15 minutes
Magnesium peroxide	.528– .289	.444	3 hours
Silicon oxide	.528– .266	.444	12 hours
Silicon dioxide	.528– .241	.435	2 hours
Strontium oxide	.528– .338	F .415– .390	1 minute
Strontium peroxide	.528– .306	F .444– .397	2 hours
Zinc oxide	.528– .438	.468	(?)
	.438– .361	F .411– .384	

[1] The substances used were all of a chemically pure grade except as otherwise noted.
[2] The presence of vapor lines makes these values uncertain.

TABLE XXIII—*Substances giving spectra*—Continued

Substance				Band limits (μ)	Band maximum (F = Flat)	Exposure
Phosphores, L and K No.	Activator	Solvent	Flux			
20	Bi	Ba	$K_2B_6O_{10}$	0.522–0.460	0.481	15 minutes
				.460– .319	.426	
16	Bi	Ba	$Na_2B_4O_7$	.513– .262	F 0.410– .361	(?)
24	Cu	Ba	NaCl	.522– .334	.470	30 minutes
37	Cu	BaS 70 p.ct. SrS 30 p.ct.	Li_3PO_4	.528– .366	.507	2 minutes
27	Sb	Ca	$Na_2SO_4.NaF$	.535– .342	.464	10 seconds
12	Bi	Ca	Li_2SO_4	.528– .399	F .475– .435	2 minutes
				.399– .351	.394	
3	Bi	Ca	$Na_2SO_4.CaF_2$	.579– .407	F .475– .439	5 minutes
			$Na_2B_4O_7$	.407– .361	.390	
32	Cu	Ca	Li_2SO_4	.535– .303	F .464– .410	5 seconds
4	Cu	Ca	$Li_2SO_4.CaF_2$	.545– .346	.419	10 minutes
29	Pb	Ca	$Na_2SO_4.NaF$	.528– .415	F .475– .435	1 minute
				.415– .341	F .393– .369	
				.341– .258	.334	
5	Mn	Ca	$Na_2SO_4.CaF_2$	.528– .393	.462	1 minute
43	CuBi	CaS	$Li_2SO_4.CaF_2$	vis.[1] – .274	F .475– .381	2 minutes
44	BiSb	CaS	$Na_2SO_4.NaF$	.528– .404	.464	20 seconds
				.404– .351	.390	
				.351– .279	.342	
39	CuBi	CaS 30 p.ct. BaS 50 p.ct. SrS 20 p.ct.	Li_3PO_4	.528– .306	F .464– .440	10 seconds
41	Cu	CaS 33 p.ct. BaS 33 p.ct. SrS 33 p.ct.	$Li_3PO_4.Li_2SO_4$	.528– .342	.449	10 seconds
36	Bi	CaS 33 p.ct. SrS 66 p.ct.	Na_2SO_4	.528– .415	F .460– .447	10 seconds
				.415– .342	.393	
31	Bi	Sr	Li_3PO_4	.528– .444	.466	2 minutes
				.444– .346	.390	
13	Bi	Sr	Na_2SO_4	.522– .425	.475	4 minutes
				.425– .349	.390	
34	Bi	SrCa	Na_2SO_4	.528– .351	.458	1 hour
2	Cu	Sr	CaF_2	vis.[1] – .351	.459	1 minute
23	Cu	Sr	$K_2B_6O_{10}$	.522– .312	F .486– .454	10 seconds
11	Cu	Sr	KH_2PO_4	.528– .384	.472	1 second
14	Cu	Sr	$KH_2PO_4.K_2B_6O_{10}$	.513– .326	.460	15 minutes
21	Cu	Sr	Li_3PO_4	.522– .406	.464	2 minutes
				.406– .342	.397	
17	Cu	Sr	$MgHPO_4$	.528– .351	.462	20 seconds
28	Ag	Sr	$Li_2SO_4.Li_2CO_3$	.528– .332	F .444– .361	10 minutes
30	Ag	Sr	Na_2SO_4	.528– .393	F .454– .435	10 minutes
				.393– .356	.390	
9	Zn	SrS	KPO_3	.522– .415	.475	2 minutes
				.415– .351	F .397– .387	
7	Zn	Sr	CaF_2	.513– .283	F .486– .384	10 seconds

[2] Vis. signifies that the band extended into the visible spectrum.

TABLE XXIII—*Substances giving spectra*—Continued

Activator	Solvent	Band limits (μ)	Band maximum (F = Flat)	Exposure
RARE EARTHS:				
Dysprosium	CaO	0.523–0.279	0.484	10 minutes
			.444	
			.437	
			.420	
			F 0.393– .361	
Europium	Al_2O_3	.528– .274	.394	35 minutes
Europium	CaO	.513– .254	F .405– .347	10 minutes
Samarium	CaO	.523– .246	.370	15 minutes
Terbium and dysprosium	CaO		.484	5 minutes
			.440	
			.420	
		.398– .352	.380	
			.364	
Terbium	$NaPO_3$	Darkening ends at	.479	2½ hours
Yttrium	CaO	.523– .304	.347	7 minutes
		.304– .225	.266	

Substance	Band limits (μ)	Band maximum (F = Flat)	Exposure
MISCELLANEOUS COMPOUNDS:			
Anthracene	0.516–0.475	0.494	11 seconds
	.475– .433	.447	
	.433– .400	.425	
Barite	.488– .245	.314	2 hours
Barium sulphate	.528– .235	(?)[1]	3 hours
Borax	.528– .256	.384	13 hours
Cadmium (ammonium) bromide[2]	.506– .326	.450	Short
Cadmium phosphate (white)	.528– .300	.444	2½ minutes
Cæsium alum sulphate	.528– .225	.427	3 hours
Calcium sulphide	.528– .351	.469	3 hours
Fluorite	.502– .460	.476	20 seconds
	.460– .444	.454	
	.444– .426	.437	
	.426– .406	.414	
	.406– .393	.398	
	.393– .370	.380	
	.370– .229	.312	
Lead sulphate	.528– .266	.397	20 minutes
Potassium bromide	.528– .238	F 0.454– .415	3 hours
Potassium fluoride	.499– .251	.390	5 minutes
Potassium iodate	.528– .294	.458	12 hours
Potassium iodide	.523– .352	.450	(?)
	.352– .266	.342	

[1] The presence of vapor lines makes this value uncertain.

[2] Cadmium ammonium bromide was heated to its boiling-point before use. The visible white fluorescence faded rapidly.

TABLE XXIII—*Substance giving spectra*—Continued

Substance	Band limits (μ)	Band maximum (F = Flat)	Exposure
Potassium uranyl nitrate $K_2UO_2(NO_3)_4$	Narrow	0.485	10 seconds[1]
Quartz window[2]	0.513–0.391	.448	12 hours
Sodium fluoride	.499– .300	.372	10 minutes
	.300– .227	.262	
Sodium periodate	.528– .326	.444	3 hours
Strontium nitrate	.528– .334	F .444– .383	15 minutes
Strontium phosphate	.513– .326	.454	30 minutes
Willemite No. 106	.528– .283	.410	20 minutes
	.283– .264	.281	
	.264– .251	.257	
	.251– .240	.244	
Zinc bromide	.506– .326	.450	33 minutes
Zinc carbonate	.528– .289	.390	45 minutes
Zinc silicate	.499– .227	.342	40 minutes
Zinc sulphate	.520– .351	.426	4 hours
	.351– .270?	.312	
	.270?– .225	F .244?– .230?[3]	
Zinc sulphide	.528– .437	.473	22 minutes
	.437– .361	F .400– .380	

[1] Due to rapid fading in the visible this exposure is composed of a number of short exposures taken at short intervals. A 17-min. continuous exposure was no better than this one.

[2] This was taken through the edge of the window, the fluorescence being much brighter in that position. An exposure for a similar time taken straight into the window gave very little blackening.

[3] The presence of vapor lines makes these values uncertain.

TABLE XXIV—*Substances giving no spectra*

[Exposures, in parentheses, are given in hours except where noted]

Antimonious oxide (Sb_2O_3)
Bismuth oxide (3)
Cadmium carbonate (3)
Cadmium oxide (3)
Cadmium sulphide (3)
Cadmium uranyl acetate (short)[1]
Cæsium uranyl chloride crystal (1)
Calcium peroxide (3)
Ceric oxide, CeO_2 (2)
Cobaltous oxide, CoO (11)
Chromic oxide, Cr_2O_3 (12)
Copper mercuric iodide (2 min.)[2]
Cupric oxide CuO (12)
Cupric sulphate $CuSO_4$ (2½)
Cuprous oxide Cu_2O (11)
Ferrous oxide, FeO (10)
Fluorescein, red, specially pure (2)[2]
Fluorescein, yellow, specially pure (14)[2]
Lead chromate (12)
Lead oxide, PbO (11)
Magnesium phosphate, dibasic (14)
Manganese dioxide, MnO_2 (11)
Mercurous chloride (2½ min.)[2]
Molybdenic acid (10 min.)[3]
Molybdenite, pure synthetic
Nickelic oxide, Ni_2O_3 (11)
Nickelous oxide, NiO (10)
Potassium bichromate, $K_2Cr_2O_7$ (½)
Silver nitrate (3)[4]
Silver sulphate (1)[5]
Sodium nitrate (4)
Stannous chloride (3)

[1] This substance fluoresced a brilliant green when first bombarded, but the fluorescence disappeared in about one-half second. It reappeared, however, as brilliantly as ever after a short cessation of bombardment.

[2] These substances scattered through the tube when the bombardment was started, and in most cases covered the quartz window so that further exposure was useless. The fluoresceins did not scatter immediately, and hence long exposures were given.

[3] A cathode vacuum could not be maintained because of a gas which was emitted.

[4] The silver nitrate after bombardment was covered with particles showing metallic luster.

[5] Silver sulphate gave a white flash when first bombarded. This also faded rather quickly. After bombardment it was covered with particles showing metallic luster.

TABLE XXIV—*Substances giving no spectra*—Continued

Stannous oxide, SnO (11)
Stannous phosphate (5)
Tellurous oxide, TeO_2
Telluric acid and chromic oxide, $H_2TeO_4Cr_2O_3$ (3)
Thorium oxide (1)[1]
Titanium dioxide (12)
Tungstic acid (3)
Uranic oxide, UO_3 (12)

[1] The oxide was produced from the nitrate by heating.

CATHODO- AND X-RAY FLUORESCENCE COMPARED

When we compare the location of the crests in the foregoing tables with the corresponding data by Perrine (see tables XVIII and XIX) there appears at first glance to be no systematic relationship. Even where a series of well-defined bands are listed, as in the case of KCl, the crests occurring under the conditions of Perrine's experiments, with X-rays as the source of excitation, do not coincide with those observed by Northrop. Nevertheless, these bands, as depicted in figure 40, are suggestive of the existence of intervals of constant frequency, and it is only necessary to take the wave-numbers to four places and their differences to make the existence of such an interval evident. All but the last band in column (1) of table XXV are equidistant, as to wave-numbers, within the error incident to determining their wave-length from the curves in Northrop's paper. The average interval is 208, which is 4×52.1, with an average departure of 2 frequency-units. Moreover, if, as in column (3) of table XXV, we introduce Perrine's values for KCl under X-rays, we find that they may be regarded as members of the same set. We may say therefore that *the spectrum of the ultra-violet fluorescence of KCl under cathodo-excitation is essentially identical with that of the same compound under X-rays,* although under the conditions of these measurements there are no coincident crests.

TABLE XXV—*The frequency intervals between crests in the spectrum of ultra-violet fluorescence of KCl*

Cathodo-excitation (Northrop)		Cathodo- and X-ray crests in single set	
(1) $1/\mu \times 10^3$	(2) Δ	(3) $1/\mu \times 10^3$	(4) Δ
4,338		3,300 (N)	
	206 = 4×51.4		155 = 3×51.5
4,132		3,145 (P)	
	210 = 4×52.4		49 = 1×49.0
3,922		3,096 (N)	
	205 = 4×51.2		51 = 1×51.0
3,717		3,045 (P)	
	208 = 4×52.1		300 = 6×50.0
3,509		2,745 (P)	
	209 = 4×52.2		257 = 5×51.7
3,300		2,488 (N)	
	204 = 4×51.1		243 = 5×48.3
3,096		2,245 (P)	
	608 = 12×50.7		
2,488			

The fact that into the list of frequencies in table XXV those belonging to the X-ray fluorescence, as deduced from the measurements of Perrine (table XX), may be interposed and from a part of the *same set,* may serve to strengthen the validity of both.

A comparison of Northrop's work on sodium chloride with that of Perrine leads to a result similar to that presented in table XXV, but there are two sets of bands, as is commonly the case with fluorescence spectra, having the same or very nearly the same frequency-interval. This interval, within the errors of observation, coincides with the Tanaka interval for sodium (70.0). The bands found by Perrine, marked P in table XXVI, columns 3 and 4, are all members of set II.

TABLE XXVI—*Frequency intervals between crests of NaCl*

Set 1. Cathodo-excitation, Northrop		Set 2. Cathodo- and X-ray crests in single set	
(1) $1/\mu\times10^3$	(2) Δ	(3) $1/\mu\times10^3$	(4) Δ
4,237		3,997 (P)	
	139=2×69.4		280= 4×70.0
4,098		3,717 (N)	
	207=3×69.0		567= 8×70.9
3,891		3,150 (P)	
	419=6×69.8		560= 8×70.0
3,472		2,590 (N)	
	282=4×70.1		141= 2×70.5
3,190		2,449 (P)	
			699=10×69.9
		1,750 (P)	

For willemite values deduced from Northrop's curves give the set in table XXVII.

TABLE XXVII—*Willemite 106a*

$1/\mu\times10^3$	Δ
4,098	
	207= 5×41.4
3,891	
	443=11×40.3
3,448	
	1,009=25×40.4
2,439	
	Average interval..40.7

The above average differs but 0.2 of a frequency-unit from that of Perrine for the same sample of willemite (40.9) as given in table XX; but Perrine's set lies about midway between the members of Northrop's set in table XXVII.

The general conclusion to be drawn from these comparisons would seem to be that while X-rays tend to develop a different set of bands, *the structure of the fluorescence spectra in the ultra-violet is essentially identical, whether excited by X-rays or by cathode rays.*

IV. NEW ABSORPTION BANDS IN THE ULTRA-VIOLET

[Describing experiments by L. J. Boardman]

The following account of work by Dr. Boardman, which is taken almost verbatim from his recent paper,[1] is of four-fold interest from the point of view of the present memoir.

(1) Many absorption bands in the spectrum of the uranyl salts are added by this photographic process to those previously determined visually.

(2) These bands are found to belong without exception to the various sets in the visible spectrum already described.[2]

(3) The new method of detecting the presence of absorption bands by the increased fluorescence excited in regions where the greatest absorption occurs is here fully and successfully developed and utilized for the first time (the original experiment upon which it is based is described in Chapter I of this treatise).

(4) The photographic method, to the application of which the present chapter is devoted, is here shown to be capable of revealing the submerged and overlapping components of an apparently continuous spectrum.

The purpose of this investigation was to study the behavior of different portions of the ultra-violet spectrum as regards the ability of exciting fluorescence. The major part of the previous work in fluorescence has been confined to a study of the fluorescence and absorption spectra of various materials and the relations between the two. This enables one to describe the phenomena, or state what happens as the result of the mechanism producing fluorescence. It also throws some light on the nature of the mechanism itself.

It seemed probable that something could also be learned about this mechanism by studying the means by which it is set in operation, in other words, by studying the conditions and means by which fluorescence is excited. As a part of this problem it is of interest to determine what wave-lengths are effective in excitation and what relations exist between the excitation, absorption, and the fluorescence spectra. Almost the only work that has been done along this line is that of Stokes,[3] and, for a certain group of material, the work of Lenard.[4]

[1] Boardman. Physical Review (2), XX, p. 552.
[2] Nichols and Howes. Carnegie Inst. Pub. No. 298.
[3] Stokes. Phil. Trans., p. 463, 1852.
[4] P. Lenard. Ueber Lichtemission und deren Erregung, Annalen der Physik, 31, p. 641, 1910.

The method of the present investigation is similar to that used by Stokes. Quartz was, however, used in place of glass, and better sources of ultra-violet light were employed. Figure 41 shows the arrangement of the apparatus. Light from the source *S* passed through a spectrograph, and then fell upon the fluorescent substance mounted in the plane of the plate-holder of the spectrograph at *A*.

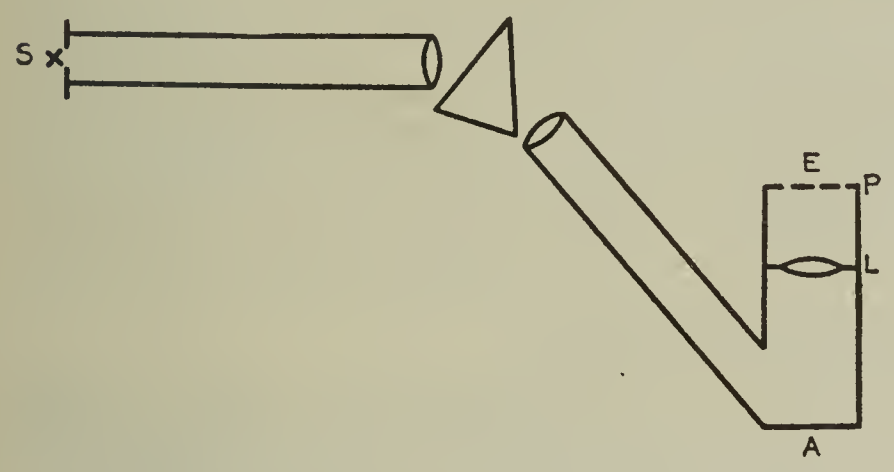


FIG. 41—Apparatus used by Boardman

With the room darkened the fluorescence was studied for color and relative intensity by the eye at *E*. For more accurate study a photograph was taken by means of a camera lens *L* and a plate at *P*. In this way the exciting power of any region of the ultra-violet light was easily determined, since the dispersed light fell immediately upon the specimen spread out to intercept the entire beam of light.

It was necessary to use a light source which gives a continuous ultra-violet spectrum as free as possible from lines or bands. An electric spark under water was quite satisfactory for a large range of ultra-violet spectrum. Other sources of light could be used to better advantage, however, in the visible and near ultra-violet region, since it was very difficult to maintain a spark in water for a sufficiently long time to give a proper exposure for the regions of weak fluorescence. Some photographs were, however, obtained by long excitation by the spark. By the method of producing the under-water spark used in this work, it was possible to maintain a vigorous spark-discharge 8 mm. in length for half an hour in distilled water, by means of a Tesla coil operated by a transformer of 1 kilowatt capacity.

It was found that a 400 c. p. nitrogen-filled glass-bulb mazda lamp gave sufficient intensity in the near ultra-violet, and this was used when possible because of its greater convenience. For somewhat shorter wave-lengths a similar lamp with a quartz bulb was used.

Two spectrographs were used: the Fuess type, which gives a spectrum about 5 cm. long, range 0.580μ to 0.200μ, and a Hilger instrument which gives five regions (5 settings) of the spectrum with a total length of about 30 cm., range 0.800μ to 0.205μ. This spectrograph, which proved to be excellent for the purpose, is constructed so that five adjustments of its parts can be made for each of the five ranges or parts of the spectrum. The ranges are: 0.800 to 0.400, 0.400 to 0.305, 0.305 to 0.255, 0.255 to 0.225, and 0.225 to 0.205. The five adjustments are: position of collimating lens, angle at which the

prism is set, the angular position of the arm carrying the plate-holder, the position of the objective lens, and the angle which the plane of the plate-holder makes with the axis of the plate-holder arm. The data furnished by the makers for the various adjustments were corrected for this particular instrument and plotted in such a way as to show the relation between each variable and the corresponding range. It was found that practically linear relations existed, so that it was possible to set for any intermediate range desired by merely interpolating between the given settings. A split quartz prism was used.

PRELIMINARY STUDY

A visual study of a great number of substances was made in order to find out what parts of the ultra-violet spectrum were most capable of exciting fluorescence, and also what substances respond best to such excitation, and were therefore suitable for further study. The Fuess spectrograph was mounted in such a way as to make the plane of the plate-holder horizontal. The substance was spread out on a piece of glass or stiff paper and held in the plane of the plate-holder. The following substances were examined in this way, a record being made in each case of the amount and position of the fluorescence excited by the ultra-violet *only*[1] (since the dispersion in this region was good, whereas the visible part was very narrow). The uranyl compounds exhibited the strongest fluorescence. They are given in the order of relative intensity, the first being the brightest.

TABLE XXVIII—*Response to ultra-violet excitation.*

STRONG RESPONSE[2]

Rubidium uranyl nitrate	Ammonium potassium uranyl chloride
Rubidium uranyl sulphate	Cæsium uranyl chloride
Potassium uranyl sulphate	Lithium uranyl acetate
Potassium uranyl nitrate	Cadmium uranyl acetate
Potassium uranyl chloride	Barium uranyl acetate
Lead uranyl acetate	Uranyl acetate
Ammonium uranyl nitrate	Sodium copper uranyl acetate
Mercury uranyl acetate	Silver uranyl acetate
Calcium uranyl acetate	Uranyl tellurate
Strontium uranyl acetate	Stannous uranyl sulphate

[1] The following uranyl compounds were found to fluoresce most strongly under X-ray excitation: Rubidium uranyl nitrate, rubidium uranyl sulphate, cæsium uranyl chloride, and lithium uranyl acetate.

[2] Given in the order of relative intensity.

TABLE XXVIII—*Response to ultra-violet excitation*—Continued

GOOD RESPONSE	FAINT RESPONSE
Anthracene[1] Phenolphthalein[1] Calcium tungstate[2] Phosphorescent willemite[2] Fluorescein[2, 3] Eosin[2, 3]	CaC_2O_4 Zinc silicate Zinc sulphate Cadmium phosphate Phosphorescent calcite Sodium uranyl cobalt acetate Sodium molybdate

PRACTICALLY UNAFFECTED

Barium chloride	Naphthol yellow	Al_2O_3	MgO
Barium sulphate	Potassium iodide	BaO	MnO
Berylium chloride	Rubidium chloride	Bi_2O_3	NiO
Calcium fluorspar	Sodium chloride	CaO	Ni_2O_3
Calcium sulphate	Sodium silicate	CeO_2	Sb_2O_3
Cadmium iodide	Telluric acid	CeO	SiO
Cæsium chloride	Thallium sulphate	Cr_2O_3	SnO_2
Didymium chloride	Tungstic acid	CuO	TeO_2
Lead chloride	Vanadium chloride	FeO	UO_3
		PbO	ZnO

[1] Variable but continuous excitations between 0.550 and 0.200μ.
[2] Excitation between 0.550 and 0.350μ and between 0.325 and 0.225μ approximately.
[3] Dissolved in water or alcohol.

Three general types of excitation were observed. First, a broad continuous region of excitation, somewhat variable in intensity and becoming gradually weaker farther out in the ultra-violet. Second, strong in the violet and near ultra-violet to about 0.350μ, where the fluorescence seems to disappear over about 0.025μ, then to reappear over a region about 0.100μ long with a maximum at about 0.275μ. Third, strong in the violet and near ultra-violet to about 0.350μ, where the intensity drops very rapidly to practically zero in some cases or to a relatively small value beyond which point the intensity gradually fades away. No fluorescence was observed beyond 0.200μ. Anthracene is a good example of the first type, calcium tungstate and fluorescein are good examples of the second type, and the uranyl compounds illustrate the third type.

Photographs were obtained of the fluorescent light emitted from nearly all of the substances listed above which show any appreciable effect. The means of mounting the material is described in the following paragraph. It was very difficult to secure good photographs in some cases, particularly with the liquid solutions of fluorescein and eosin. The Fuess spectrograph was used and a camera lens of 7 inches focal length. Exposures ranging from 1 minute to 30 minutes were necessary.

METHOD OF MOUNTING THE FLUORESCENT SUBSTANCE

It was necessary to have the fluorescent material offer a smooth surface to the exciting light in order to obtain a good record on the photographic plate, to which end the following simple method was used. A strip of varnish or glue about 2 centimeters wide was made across the whole width of the plate, and the powdered substance was sprinkled over this with sufficient depth to cover it completely. Another glass plate was then used to press upon and rub this surface till it was made as smooth as possible. Care was taken not to leave any part of the surface in a matte-white condition due to rubbing, as such a part may appear on a photograph to be different from its surroundings. In case of some of the uranyl salts the natural crystals are very hard to reduce to fine enough granulations to make a smooth surface possible in this way. Some of the photographs show this. In case of liquids or solutions a strip of quartz was used, and it was mounted in such a way as to cover the portion of liquid to be exposed.

FURTHER STUDY OF THE URANYL COMPOUNDS

It was mentioned above that the uranyl compounds were excited to fluorescence by wave-lengths of light lying between 0.550μ and 0.350μ. (Excitation by shorter wave-lengths than this was very feeble, too faint indeed to be photographed.) In the most intense part of the excitation, as photographed by the Fuess spectrograph, there appears to be a short region in which the excitation is variable, giving what might be called bands, and this region is the same as that in which absorption bands for these same materials are found. Now, fluorescence is undoubtedly due primarily to absorption, though it cannot be assumed that greater absorption will produce proportionately greater fluorescence. It seems reasonable nevertheless to expect that there may be some variation in the excitation where there is variable absorption. If it is true that the variation in the intensity of the fluorescence is due to the changing absorption of the dispersed exciting light, this method might well be used in detecting and studying the absorption of materials, for if light of a particular wave-length is absorbed and this excites fluorescence which emanates from the same, or some neighboring, spot, it would be very easy to observe this photographically in case there is good dispersion of the exciting light. The work that follows is an attempt first to test the validity of the assumption by seeing if fluorescence bands *do* occur where absorption bands are known to exist, and (if the results confirm the assumption) to locate the position of as many absorption bands as this method is capable of giving, and thereby to test the laws which have been found to govern the arrangement of the bands previously observed. The uranyl salts are particularly good for this work because

they give many narrow bands, both in the fluorescence region of the spectrum and in the absorption region. The following are the compounds tested:

1. Barium uranyl acetate
2. Lithium uranyl acetate
3. Mercury uranyl acetate
4. Strontium uranyl acetate
5. Uranyl acetate
6. Sodium copper uranyl acetate
7. Cæsium uranyl chloride
8. Potassium uranyl chloride
9. Potassium uranyl nitrate
10. Rubidium uranyl nitrate
11. Cæsium uranyl sulphate
12. Rubidium uranyl sulphate

Nichols and Howes,[1] in their recent treatise entitled "Fluorescence of the Uranyl Salts," give a summary of results showing the distribution and character of the fluorescence spectrum and the absorption spectrum of many uranyl compounds. It is shown that the spectrum of the fluorescent light consists of bands which naturally form eight groups of five members each, approximately, ranging from 0.640μ to 0.490μ, or thereabouts. The absorption spectrum consists also of bands having about the same arrangement, but ranging from 0.490μ to 0.380μ, apparently a continuation of the fluorescence spectrum. The frequency intervals (reciprocal wave-length intervals) between homologous bands of each group are practically the same throughout the spectrum of either, the interval being about 86 in the fluorescence spectrum and about 70 in the absorption spectrum. The last member of the fluorescence series is usually coincident with or at a distance from the first member of the absorption series of the homologous band of 86 or 70 frequency-units. Considering all of the series of the various homologous bands, there is an overlapping of the fluorescence and absorption spectra of about three groups, called the "reversing region," because here there are coincidences of fluorescence and absorption bands.

In this work a glass-bulb nitrogen-filled tungsten lamp, running at 6 amperes, was used as a source of ultra-violet light. A quartz mercury lamp was used[2] for calibration purposes, the calibration spectrum being photographed alongside of the other spectrum by exposing an adjacent portion of the slit of the spectrograph, both exposures taking place at the same time.

The intensity of blackening of the plates was measured by means of a device set up by J. O. Perrine in connection with his work on ultra-violet fluorescence excited by X-rays, which is described in the foregoing part of this chapter. Much of the success of the present work is due to this apparatus. The instrument, which is highly sensitive to any variation in the density of the photographic image, has many

[1] Nichols and Howes. Carnegie Inst. Wash. Pub. No. 298, 1919.

[2] The well-known yellowish-green fluorescence of these substances is of a color to which most photographic plates do not respond well. The most satisfactory of the numerous plates tested was found to be the polychrome plate made by the Eastman Kodak Company.

advantages over other methods such as those depending on the eye, but faulty places in the photograph must be carefully avoided or eliminated by comparison with other photographs.

METHOD OF PLOTTING

Curves were first made from the galvanometer deflections and the positions on the comparator. The intensities of the light transmitted by the negative were plotted as ordinates and the comparator readings as abscissæ, these plots being made while the measurements were being made, *i. e.*, plotting rather than recording the numbers. The intensities are merely relative, so that a convenient arbitrary scale was chosen to represent them. The positions of the mercury lines were located on the plot by observing the comparator reading for the smallest deflection of the galvanometer; thus the densest part of the line was taken as the proper position of the line. A setting could be made to the nearest tenth of a millimeter. Five to seven mercury lines were thus located on each plot. Knowing their wave-lengths to four significant figures, their reciprocals were plotted (on another sheet) as ordinates against their recorded positions on the plot as abscissæ, and thus a calibration plot was obtained, giving the reciprocal wave-lengths for any comparator reading on the first plot. Using this calibration plot, the final plot was obtained where the intensities of the light were plotted against the reciprocal wave-lengths. A new calibration plot was used whenever the mercury lines were found to be spaced differently, due to different magnifications caused either by a change in the settings of the spectrograph or by a change in the camera adjustment. Final curves were made in this way for each of the twelve uranyl compounds.

In the original plots a millimeter represents 2.5 frequency-units, and one-tenth of a millimeter on the photographic plate. The accuracy of the data recorded in tables XXIX and XXXIII is such that the results are probably correct to within three frequency-units. An estimated "probable error" is near one frequency-unit. Typical curves are presented, greatly reduced, in figures 42, 43, 44, and 45.

Peaks in the curves represent regions of greater fluorescence. They are undoubtedly regions of greater absorption, and many of them coincide with absorption bands of these substances that have been located by other methods. The data in the tables are arranged in two columns so as to show the agreement of the results obtained by this method and measurements made by other methods. The first column shows the former, the second column the latter, as published by Nichols and Howes. The photo-electric cell is so sensitive as to detect bands that are not apparent to the unaided eye. Data for these fainter bands seem to check equally well; therefore credence

is given to these also. Wherever there is a marked difference in the direction of the curve such as to indicate a partially resolved band, and wherever the main part of an unresolved band appears, there is

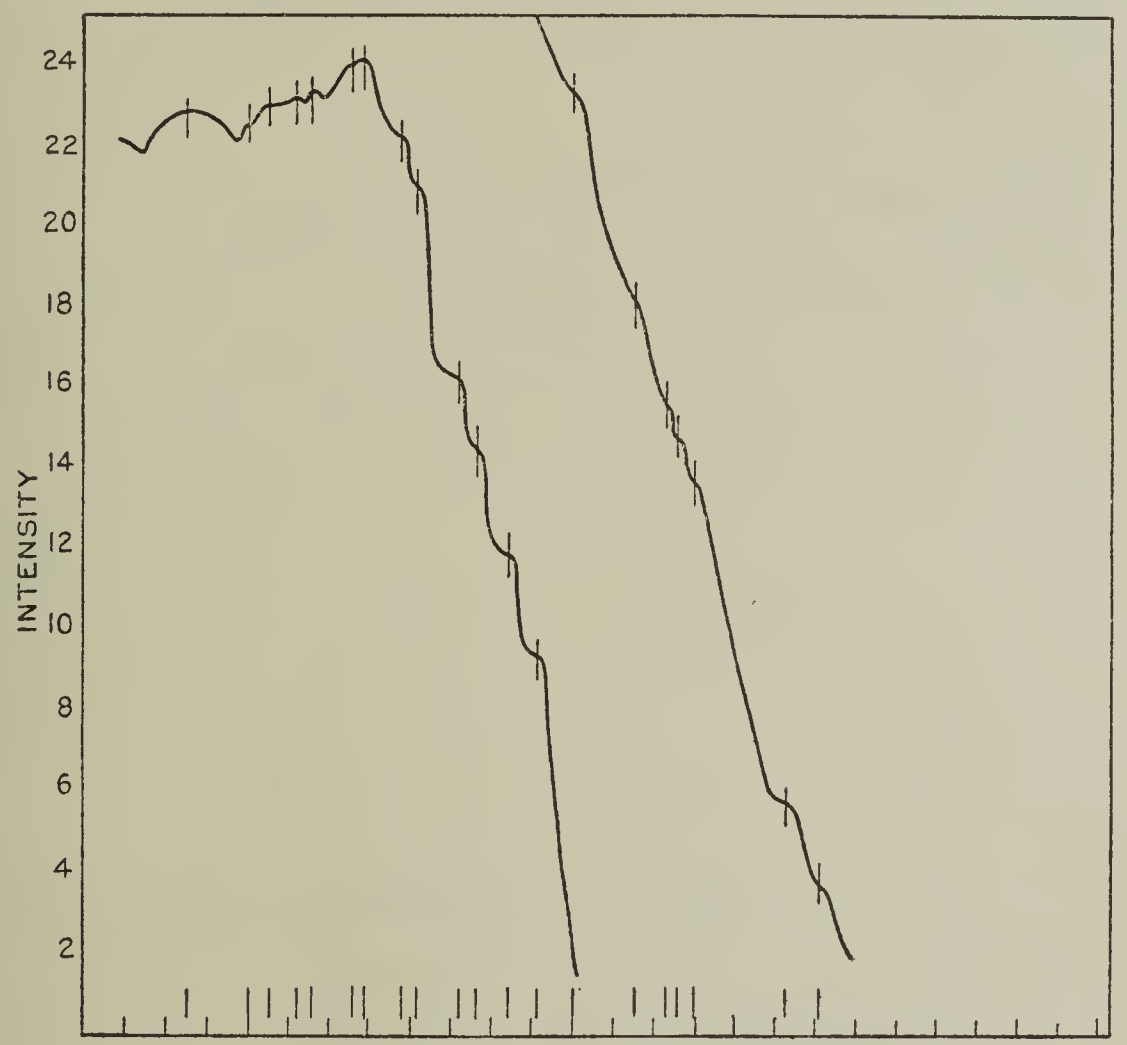


FIG. 42—Submerged components in the absorption spectrum of lithium uranyl acetate (ultra violet)

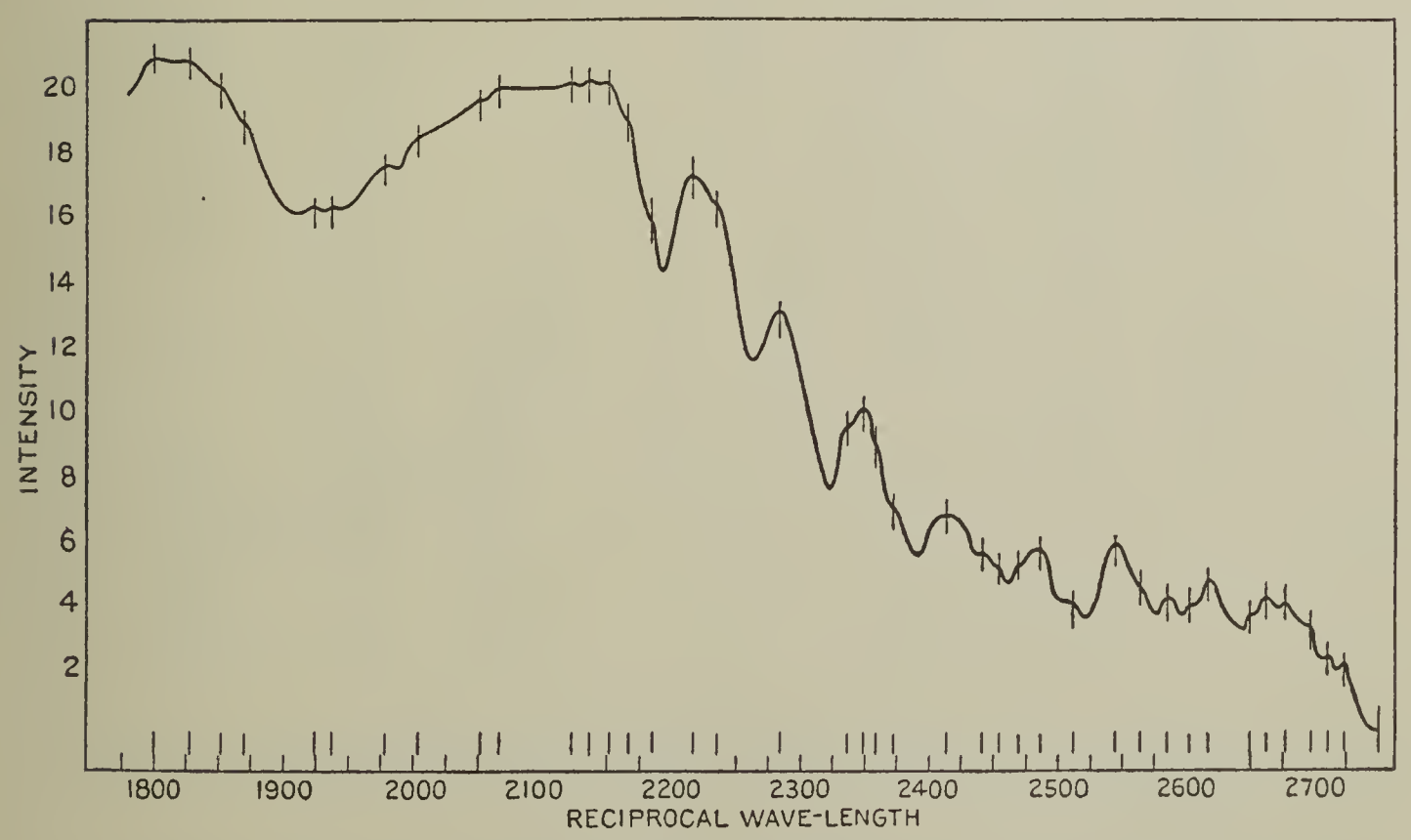


FIG. 43—Submerged components in the absorption spectrum of lithium uranyl acetate (visible)

a short vertical line drawn through the curve, and these lines appear again at the bottom of the plot. The bands have been designated by the same symbols used by Nichols and Howes. In cases where bands could not be identified, symbols were assigned so as to agree

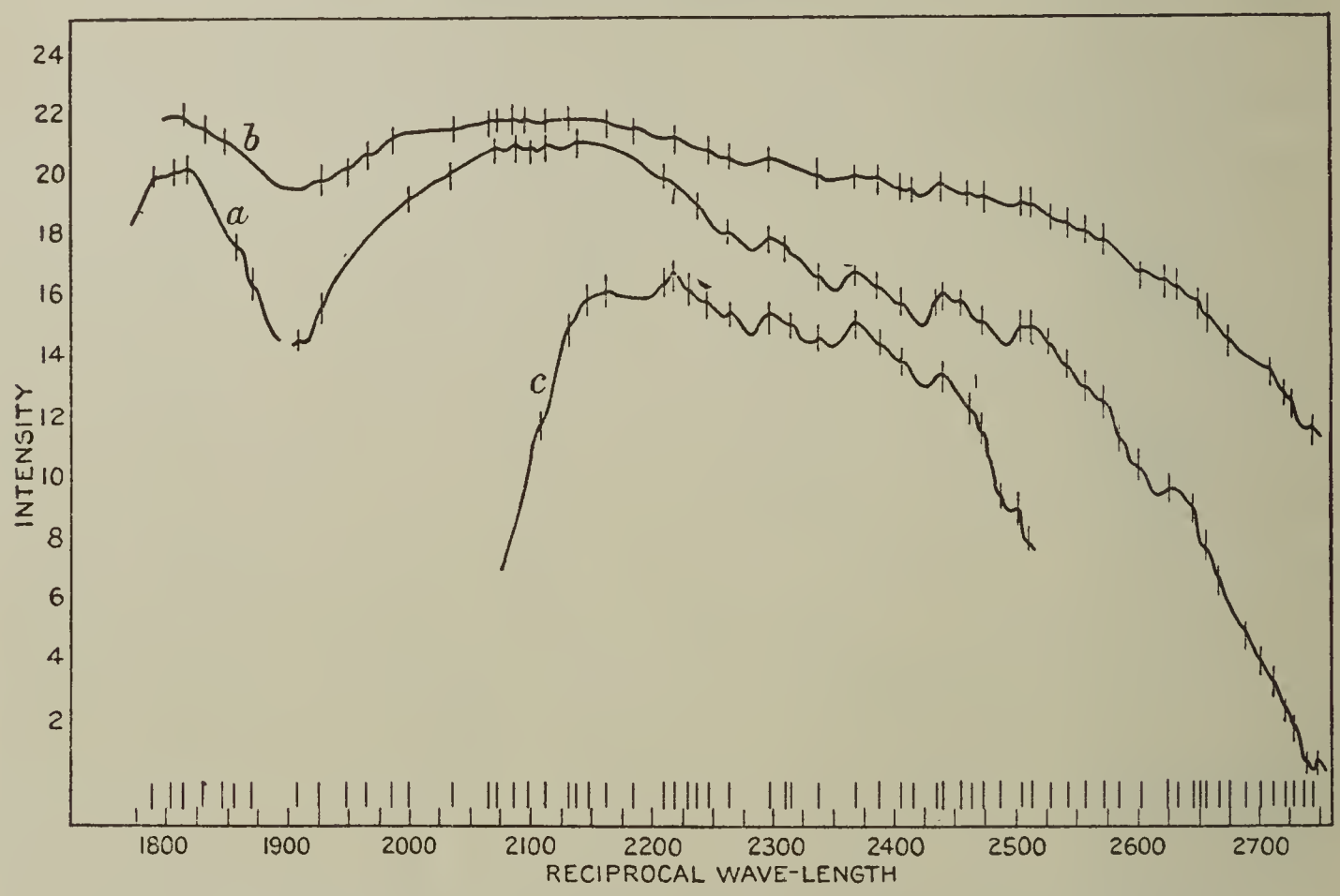


FIG. 44—Submerged components in the absorption spectrum of cæsium uranyl chloride (visible)

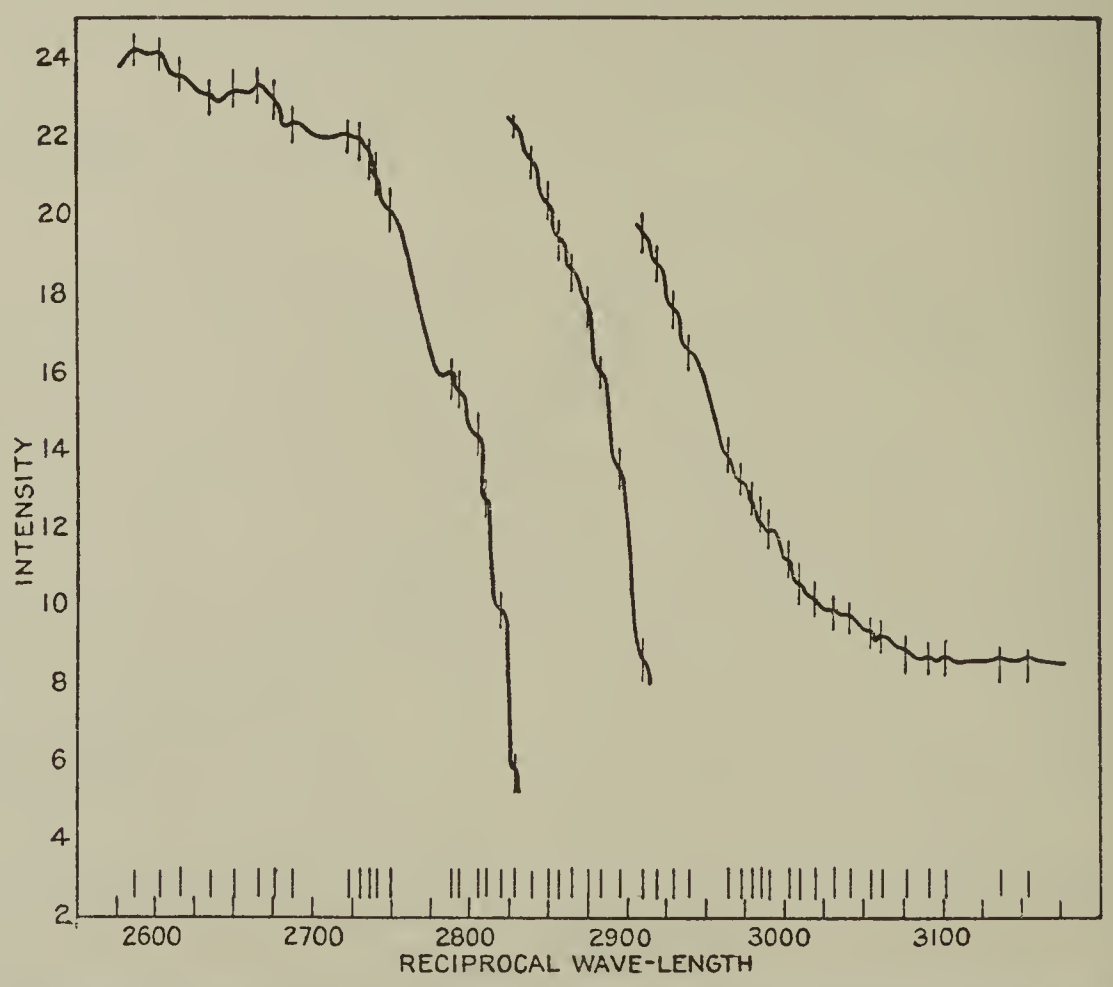


FIG. 45—Submerged components in the absorption spectrum of cæsium uranyl chloride (ultra violet)

as nearly as possible with those of the same class, *e. g.*, the acetates, nitrates, etc., as determined by Nichols and Howes.

EXTENSION OF THE ABSORPTION REGION

Some of the photographs show very distinctly that the absorption bands extend farther into the ultra-violet region than it has been possible to go by the other methods. Cæsium uranyl chloride is particularly rich in bands throughout the region covered by the photograph. It has been shown[1] that this substance is more fully resolved at ordinary temperatures than most of the other uranyl compounds. In order to see if the bands really extend as far as there is any fluorescence excited, a few long-time exposures were made, the range being 0.390μ to 0.310μ. A quartz-bulb nitrogen-filled tungsten lamp was used. An exposure of two hours was found to be sufficient to register all of the bands that could be recorded by the photographic plate. Further exposure only made the black part of the plate darker and made the detection of the bands by the photo-electric cell more difficult. In fact, it was necessary to have regard to the time of exposure in all cases in order to obtain proper sensitiveness in measuring the plates. Too long exposures tend to fill up the places between the bands and destroy the contrast.

TABLE XXIX—*Bands appearing in two or more curves for cæsium uranyl chloride*

Range 0.550μ to 0.370μ approximately. See fig. 44.

	Curve *a*, 1/λ	Curve *b*, 1/λ	Curve *c*, 1/λ	Curve on fig. 45		Curve *a*, 1/λ	Curve *b*, 1/λ	Curve *c*, 1/λ	Curve on fig. 45
B_1	1,812	1,810	.....	.....	d_2	2,440	2,438	2,440	.....
D	1,925	1,925	.....	.....	a_1'	.....	2,462	2,464	.....
E_2'	2,032	2,035	.....	.....	b_2'	2,473	2,475	2,473	.....
d	2,070	2,072	.....	.....	d_2'	2,505	2,505	2,503	.....
d′	2,086	2,085	.....	.....	d_2	2,512	2,512	2,510	.....
e_2'	2,098	2,095	.....	.....	e_2''	2,528	2,530	.....	.....
b	2,113	2,113	.....	.....	b_2'	2,543	2,543	.....	.....
b_3	.....	2,131	2,130	.....	b_3	2,557	2,557	.....	.....
d	.....	2,148	2,145	.....	d_1''	2,572	2,572	.....	.....
d_2''	.....	2,162	2,162	.....	d_2	2,586	.....	.....	2,586
d′	2,210	.....	2,210	.....	e_2''	2,600	2,602	.....	2,602
d	.....	2,218	2,218	.....	c	.....	2,632	.....	2,633
e_2''	.....	2,245	2,245	.....	d	.....	2,650	.....	2,650
b_2'	2,263	2,263	2,265	.....	e	2,657	2,657	.....	.....
d_2'	2,298	2,296	2,297	.....	a	.....	2,675	.....	2,675
b_2	2,337	2,336	2,337	.....	b_2'	2,687	.....	.....	2,686
d_2	2,367	2,365	2,368	.....	d_1''	2,712	2,710	.....	.....
e_2''	2,385	2,388	2,388	.....	d	2,722	2,722	.....	2,722
b_2'	2,405	2,405	2,405	.....	e	2,730	2,728	.....	.....

All of the twelve compounds were photographed for the range 0.390μ to 0.310μ, measurements were made, and the data plotted in the

[1] Nichols and Howes. Fluorescence of the Uranyl Salts, 1919, Carnegie Inst. Wash. Pub. No. 298, p. 61.

same manner as in the case of the first (visible) range. Since the first range extended from about 0.550μ to 0.370μ, there was an overlapping of about 0.020μ. This repetition aided in establishing the reality of the bands. Only for cæsium uranyl chloride were there independent measurements made with the photo-electric cell from different photographs over the first range. These are plotted on the same sheet (fig. 44). There is also a curve to show the effect of placing a screen between the substance and the plate with the hope of screening off some of the visible light diffusely reflected from the substance. This procedure was, however, not satisfactory. One purpose of the three plots (or curves) for cæsium uranyl chloride is to show how well the bands check. The data are given in table XXIX. Bands that appear in two or more curves are given in parallel columns. It can be seen that the differences are few in number and are well within the experimental error.

TABLE XXX[1]—*Absorption bands found by Boardman (B); by Nichols and Howes (N and H).*

Barium uranyl acetate		Lithium uranyl acetate		Uranyl acetate	
B. values of 1/λ	N. and H. values of 1/λ p. 161, 167	B. values of 1/λ	N. and H. values of 1/λ, p. 158, 164	B. values of 1/λ	N. and H. values of 1/λ, p. 149
1,805 I		1,800 A		1,788 E_1	1,791 E_1
1,830 D	1,828 D	1,827 C	1,825 C	1,803 F	1,802 F
1,862 H		1,852 F	1,852 F	1,820 G	1,817 G
1,888 I		1,870		1,860 B	1,857 B
1,925 E	1,923 E	1,924 D		1,913 H	1,912 H
1,943 G	1,942 G	1,938 F	1,936 F	1,965 E	1,965 E
1,975 I		1,980 I		1,988 G	1,989 G
2,018 F	2,017 F	2,005 D	2,005 D	2,028 B	2,029 B
2,032 H		2,052 h		2,039 C′	2,039 C′
2,070 C		2,068 h′		2,053 F_1	2,056 F_1
2,085 D	2,086 D	2,125 h	2,124 h	2,075 G	2,073 G
2,100 F	2,101 F	2,138 h′		2,088 H	
2,125 G′		2,152 c′		2,100 e′	
2,155 c		2,168 c		2,120 f′	
2,210 g′		2,185 e	2,185 e	2,150 d	
2,245 e′		2,219 c′		2,173 e′	
2,275 gh	2,276 gh	2,238 c	2,235 c	2,210 i	
2,305 c″		2,285 c		2,215 g	
2,345 gh		2,338 h		2,223 d	
2,365		2,350 h′		2,260 f′	
2,395 e	2,394 e	2,360 c′		2,270 k	
2,420 gh	2,419 gh	2,373 c	2,373 c	2,281 i	
2,450 f′		2,415 h′		2,303 c	
2,475 g		2,443 c	2,446 c	2,315 e′	
2,488 gh	2,487 gh	2,455 f		2,323 e	
2,502 c		2,470 e		2,340 k	
2,520 f′		2,488 h′		2,353 d	
2,530 e″		2,513 c	2,515 c	2,388 f	
2,548 g		2,545 h		2,412 k	
2,560 gh		2,565 c		2,445 c	
2,568 c′		2,586 c	2,585 c	2,465 e	

[1] Page numbers refer to Carnegie Inst. Pub. No. 298.

TABLE XXX—*Absorption bands found by Boardman (B); by Nichols and Howe (N. and H.);*—Continued

Barium uranyl acetate		Lithium uranyl acetate		Uranyl acetate	
B. values of 1/λ	N. and H. values of 1/λ, p. 161, 167	B. values of 1/λ	N. and H. values of 1/λ p. 158, 164	B. values of 1/λ	N. and H. values of 1/λ, p. 149
2,578 c		2,603 g		2,490 i	
2,600 e″		2,610 e		2,503 d	
2,615 g		2,618 h		2,518 c	
2,626 h′		2,635 c		2,538 e	
2,632 gh		2,650 c		2,547 f′	
2,665 e′		2,663 c		2,557	
2,688 g		2,678 e		2,563 i	
2,707 c′		2,688 h		2,576 d	
2,728 f′		2,698 h′		2,585 c	
2,738 e′		2,711 c′		2,593 e′	
2,748 e		2,724 c		2,602 f	
2,757 g		2,743 g		2,607 e′	
2,770 gh		2,750 e		2,618 f′	
2,790 c″		2,778 c		2,633 i	
2,805 e′		2,790 c		2,638 g	
2,815 e		2,810 g		2,653 c	
2,843 gh		2,828 h		2,675 e	
2,855 c		2,850 c′		2,680 x	
2,867 f′		2,889 e		2,690 f′	
2,877 e′		2,907 h′		2,697 k	
2,888 e		2,915 c		2,708 g	
2,905 h′		2,925 c		2,718 d	
2,922 c′		2,982 c		2,740 f	
2,930 c″		3,003		2,748 x	
2,943 e′				2,763 k	
2,978 gh				2,777 g	
2,995 c				2,789 d	
3,030 e				2,813 e	
3,085 e′				2,825 f′	
3,122 c′				2,838 k	
3,148 f′				2,848 g	
				2,880 e	
				2,923 d	
				2,948 e	
				2,973 k	
				3,028 x	
				3,057 g	
				3,075 d	
				3,118 k	
				3,128 g	
				3,143 d	
				3,165 x	

DISCUSSION OF RESULTS

In tables XXX to XXXIII comparison is made with former data obtained when the substance was at the temperature of liquid air, —185° C. This seems justifiable because of the fact that some of the compounds are partially resolved at room temperature, so that the components, which are separated quite well by the relatively large dispersion of the spectrograph, show up well when measured by the photo-electric cell.

A comparison of the results obtained by the present method with those of other methods seems to establish the fact that *the position of the absorption bands can be determined by the fluorescence that the absorption gives rise to,* a fact already established by H. E. Howe[1] in the case of certain phosphorescent sulphides. Not all

TABLE XXXI[1] *Absorption bands found by Boardman (B); by Nichols and Howes (N and H).*

Potassium uranyl nitrate		Potassium uranyl chloride		Rubidium uranyl sulphate	
B.	N. and H.	B.	N. and H.	B.	N. and H.
1,795 D	1,794 D	1,761		1,810 I	1,812 I
1,823 I	1,824 I	1,787 A_1	1,785 A_1	1,822 A′	
1,860 B	1,862 B	1,815 C_1	1,816 C_1	1,842 C	1,844 C
1,978 E	1,976 E	1,945 E_2'	1,940 E_2'	1,872 F	1,872 F
2,005 J	2,007 J	1,987 C_2	1,988 C_2	1,907 A′	1,908 A′
2,070 F	2,069 F	2,012 d_3	2,014 d_3	1,948 E	1,947 E
2,093		2,085 d_3		1,957 F	1,955 F
2,127 d		2,155 d_3	2,155 d_3	1,990 A′	1,992 A′
2,162 f		2,237 e_2'		2,012 C	2,011 C
2,188 l′		2,268 c_2'	2,264 c_2'	2,063 b_1	2,066 b_1
2,268 d	2,269 d	2,335 c_2'	2,333 c_2'	2,078	
2,337 d		2,375 e_2'	2,375 e_2'	2,093 e_1	2,096 e_1
2,372 f	2,369 f	2,390 a	2,392 a	2,133 b_1	2,137 b_1
2,394 l′	2,397 l′	2,456 a_1	2,456 a_1	2,165 e_1	
2,425 j		2,468 c_2		2,190 g	2,188 g
2,450 k		2,477 c_2'		2,205 b_1	2,206 b_1
2,492 j		2,530 a_2''	2,533 a_2''	2,238 e_1	
2,522 k		2,548 c_2'		2,268 h	2,267 h
2,535 l′		2,595 a_1	2,595 a_1	2,282 c_1	
2,563 j		2,613 c_2'		2,300 d	2,301 d
2,580 f		2,626 d_1		2,322 g_1	2,322 g_1
2,605 l′		2,655 e_2'		2,340 h	2,341 h
2,618 d		2,665 a_1		2,375 e_1	2,375 e_1
2,637 j		2,675 c_2		2,410 h	2,409 h
2,655 f		2,698 d_1		2,420 b_1	
2,675 l′		2,726 e_2'		2,430 c	
2,703 j		2,737 a_1		2,450 e_1	2,450 e_1
2,722 f		2,755 c_2'		2,482 h	
2,745 l′		2,782 d_3		2,498 c_1	
2,757 d		2,800 b_1'		2,522 e_1	
2,798 k		2,807 a_1		2,550 h	
2,813 l′		2,818 c_2		2,572 c	
2,853		2,835 d_1		2,585 d	
2,883 l′		2,850 d_3		2,606 g_1	
2,898 d		2,876 a_1		2,622 h	
2,915 j		2,887 c_2		2,637 c_1	
2,928 f		2,898 c_2''		2,653 d′	
2,953 l′		2,918 d_3		2,667 e_1	
2,983 j		2,939 b_1'		2,680 g	
3,032 d		2,950 c_2		2,705 c_1	
3,050 j		2,968 c_2''		2,715 c	
3,075 k		2,998 e_2'		2,724 d	
3,100 d		3,018 a_1		2,738 e_1	
		3,402 d_1		2,745 g_1	
		3,080 b_1'		2,757 h_1	

[1]Page numbers refer to Carnegie Inst. Wash. Pub. No. 298.

[1] Trans. Am. Philos. Soc., LVI, p. 259 (1917).

TABLE XXXI—*Absorption bands found by Boardman (B); by Nichols and Howes (N and H).*—Continued

Potassium uranyl nitrate		Potassium uranyl chloride		Rubidium uranyl sulphate	
B.	N. and H.	B.	N. and H.	B.	N. and H.
		3,100 c_2' 3,128 d_3 3,151 a		2,782 c_1 2,803 2,820 g 2,838 b_1 2,855 c 2,898 h_1 2,915 c_1 2,930 c 2,949 2,978 b_1 3,000 c 3,040 h_1	

absorption bands may have the power of exciting fluorescence, and, if so, such bands would not appear on the plate. This may explain why some bands are missing by this method. Most of the known bands do appear, however, and many more besides. Where formerly the absorption spectrum was observed only between 0.490μ and 0.380μ, approximately, *the range is extended by this method in both directions, i. e.,* 0.550μ to 0.322μ, or through a frequency range of 1,800 to 3,100. In the extension toward the shorter wave-lengths the bands readily fall into the series already determined, a fact which strengthens the belief that all regions showing fluorescence really serve to locate absorption bands.

In a few instances there seemed to be a new series starting somewhere near the middle of the complete absorption region, but more observations are needed to establish this if such is the case. Series of this sort are indicated by letters in the latter part of the alphabet. Again, there is some indication that the intensity of the members of the series varies as we go through the spectrum, resulting in more than one maximum. If this is true it may explain the apparent omission of a part of the series due to the faintness of the bands, as can be noted in some cases.

REVERSING REGION

The so-called reversing region lies within the seventh, eighth and ninth groups of the fluorescent spectra, *i. e.,* 2,000 to 2,200 frequency-units, approximately. This region is extended farther toward the long wave-lengths if credence is given to the bands herein contained and if these bands are due to absorption, for, if any point on the plate containing the fluorescent material is being excited to fluorescence by the absorption of light of a particular wave-length, this

TABLE XXXII[1]—*Absorption bands in the spectra of various uranyl salts.*

Cæsium uranyl sulphate		Strontium uranyl acetate		Sodium copper uranyl acetate	Mercury uranyl acetate	Rubidium uranyl nitrate
B.	N. and H. p. 175, 178	B.	N. and H. p. 160, 166			
1,795 E	1,794 E	1,810		1,820 C	1,798 A	1,788 D
1,815 G	1,813 G	2,000 D	2,004 D	1,873 B	1,812 B	1,807 F
1,845 B	1,848 B	2,050 H	2,046 H	1,975 A	1,885 B	1,840 K
1,864 C	1,861 C	2,128 h′		2,000 D	1,980 C	1,852 L
1,903 G		2,200 h′	2,206 h′	2,040 B	2,015 c′	1,910 l
1,915 I	1,913 I	2,270 h	2,274 h	2,080 C	2,030 c	1,923 K
1,952 D	1,954 D	2,287		2,100 f	2,085 c′	1,960 D
1,990 H	1,993 H	2,302 j		2,128 b	2,150 h	2,045 D
2,018 i		2,337 h′		2,152 h	2,200 g	2,095 K
2,035 c′	2,036 c′	2,350 i	2,350 i	2,205 g	2,218 h	2,120 l′
2,050 E	2,052 E	2,400 e″	2,400 e″	2,263 f_1	2,252 e	2,193 l′
2,063 f	2,061 f	2,437 a		2,275 g	2,320 e	2,218 δ
2,080 h	2,077 h	2,516 j		2,300 h	2,365 c′	2,270 d
2,087 i	2,085 i	2,544 h′		2,340 g	2,405 h′	2,295 h
2,102 c	2,104 c	2,578 a		2,365 h	2,427 h	2,338 d
2,138 g		2,613 h′		2,410 g	2,455 d	2,360 δ
2,147 g′	2,144 g′	2,655 j		2,420 i	2,493 i	2,375 f
2,165 a	2,165 a	2,680 e″		2,473 f_1	2,514 c	2,390 l
2,192 e		2,695 h		2,538 f_1′	2,532 e	2,402 l′
2,222 g′		2,718 a		2,564 i	2,563 i	2,432 h
2,232 a		2,732 b		2,573 h	2,590 f	2,473 l′
2,280 g	2,280 g	2,770 i		2,590 f	2,602 e	2,505 h
2,290 g′		2,799 b′		2,605 f_1′	2,622 g	2,527 l
2,307 a		2,811 c		2,620 g	2,633 i	2,550 d
2,320 c′		2,820 e″		2,627 g′	2,660 f	2,570 δ
2,352 g		2,835 h		2,632 i	2,677 f_1	2,585 f
2,372 a		2,875 b		2,655 c′	2,703 i	2,595 l
2,405 e		2,903 h		2,660 f	2,707 h	2,618 d
2,428 g′	2,427 g′	2,928 a		2,675 f_1′	2,722 c	2,626 e
2,460 c′		2,945 b		2,680 f_1	2,732 f	2,635
2,480 e′		2,965 h′		2,688 g	2,738 d	2,649 x
2,500 g′	2,498[2]	2,975 h		2,703 i	2,755 h′	2,655 f
2,530 c′		3,010 b′		2,713 h	2,770 c_1	2,660 k
2,543 e	2,543[2]	3,020 c		2,728 f	2,780 h	2,670 l
2,550 e′		3,093 c		2,753 f_1	2,799 f	2,680 l′
2,568 g′	2,567[2]			2,770 i	2,823 f_1	2,698 e
2,578 i				2,780 h	2,835 g	2,712 h
2,595 c				2,793 c′	2,850 h	2,730 k
2,605 d_1				2,813 f_1′	2,898 h′	2,743
2,615 e	2,613[2]			2,835 g′	2,910 c_1	2,750 l′
2,626 f′				2,850 h	2,921 h	2,755 d
2,643 g′				2,863 c′	2,960 f_1	2,770 e
2,675 d_1				2,876	2,978 c_1	2,780 S
2,692 e′				2,903 g′	3,015 f	2,802 k
2,703 g				2,922 h	3,050 c_1	2,822 l′
2,726 a				2,934 f	3,170 f_1	2,827 d
2,756 e				2,968 g		2,835 e
2,770 g				3,005 f		2,859 x
2,789 i				3,040 g′		2,865 f
2,820				3,068 c′		2,870 k
2,850 g′				3,097 f_1		2,898 d
2,874 c				3,168 f_1		2,925 h
2,885 d_1						2,939 k
2,906 e′						2,953
2,920 g′						2,965 d
2,928 i						2,988 S
2,947 c						3,002 x
2,975 e′						3,010 k
2,993 g′						3,028 l′
3,001 i						3,045 e
3,026 d_1						3,075 f
3,052 g						3,089 l
3,068 i						3,118 e
3,133 g′						3,139 x
3,168 d_1						3,150 k
						3,173 l′

[1] Page numbers refer to Carnegie Inst. Wash. Publ. No. 298.

[2] No letters assigned.

absorption being due to the fluorescent material itself, there is evidently a reversal wherever the wave-length of the exciting light is equal to the wave-length of a band of the fluorescence spectrum. In the tables there are shown several bands agreeing well with the bands of the fluorescence spectra, *i. e.*, as well as the precision of the

TABLE XXXIII[1]—*Absorption bands in the spectrum of cæsium uranyl chloride*

B.	N. and H.	B.	N. and H.	B.
1,785 E_2'		2,405 b_2'	2,405 b_2'	2,788 d_2'
1,812 B_1	1,810 B_1	2,409 b_2	2,410 b_2	2,793 d_2
1,828 C	1,828 C	2,415 b_3	2,416 b_3	2,804 e_2'
1,845 D_1	1,843 D_1	2,435 d_2'	2,436 d_2'	2,810 e_2''
1,855 D_2'	1,854 D_2'	2,440 d_2	2,441 d_2	2,819 b
1,868 E_2''	1,866 E_2''	2,455 e_2		2,828 b_2'
1,906 B_3		2,462 a_1'		2,839 b_3
1,924 D	1,924 D	2,474 b_2'	2,476 b_2'	2,850 d
1,950 E_2''	1,950 E_2''	2,489 c		2,857 d_2'
1,963 A_2	1,964 A_2	2,505 d_2'	2,509 d_2'	2,865 d_2
1,985 B_2	1,985 B_2	2,512 d_2	2,513 d_2	2,874 e_2'
1,998 C_1	1,998 C_1	2,528 e_2''	2,530 e_2''	2,884 e_2''
2,032 E_2'	2,030 E_2'	2,543 b_2'		2,895 b_2'
2,065 c	2,064 c	2,557 b_3		2,911 c
2,070 d'	2,071 d'	2,572 d_1''		2,920 d
2,085 d_2'	2,086 d_2'	2,586 d_2	2,585 d_2	2,930 d_2'
2,098 e_2'	2,100 e_2'	2,601 e_2''		2,940 d_2''
2,107 a		2,615 b_2'		2,966 b_2'
2,113 b	2,114 b	2,625 b_3		2,973 b_2
2,131 b_3	2,132 b_3	2,632 c		2,980 b_3
2,137 c_1'	2,135 c_1'	2,645 d_2'		2,984 c
2,147 d	2,146 d	2,650 d_2		2,990 d
2,162 d_2''	2,164 d_2''	2,657 e		3,003 d_2
2,185 b	2,184 b	2,665 e_2''	2,670 e_2''	3,010 d_2''
2,210 d'	2,212 d'	2,675 a	2,674 a	3,020 e_2''
2,218 d		2,680 b		3,032 b
2,230 d_2	2,229 d_2	2,687 b_2'		3,043 b_2
2,238 e_2'	2,239 e_2'	2,693 b_2		3,055 c
2,245 e_2''	2,245 e_2''	2,702 c		3,062 d
2,263 b_2'	2,263 b_2'	2,712 d		3,077 d_2''
2,297 d_2'	2,296 d_2'	2,722 d_2		3,092 e_2''
2,310 e	2,310 e	2,730 e		3,102 b
2,315 e_2	2,314 e_2	2,736 e_2'		3,137 d_2'
2,337 b_2		2,740 e_2''		3,155 e_2'
2,368 d_2	2,369 d_2	2,748 a		
2,388 e_2''	2,389 e_2''	2,750 b		

[1] Page numbers refer to Carnegie Inst. Wash. Pub. No. 298.

work warrants. These therefore indicate more reversals than have been heretofore obtained, and that the number of reversals in any one series is not limited to one, but may be as great as two or three.

It is rather curious that most of the new reversals are on the long wave-length side of the "reversing region" as given by Nichols and Howes. In the cases of potassium uranyl chloride and rubidium uranyl sulphate none of the reversals by this method has been observed by other methods. This is true with cæsium uranyl chloride, excepting the series E_2''. The methods give results that agree in

series F of cæsium uranyl sulphate. It must be admitted, however, that more data are needed in order to confirm or disprove the existence of the new reversals. In cases where several photographs were made for the same substance there is a close agreement between the independent measurements, so that one is convinced that the method is capable of giving results quite comparable with those obtained by other methods.

Table XXXIV shows the reversals of the bands in the various substances studied. The wave-numbers in the first column are from tables XXX to XXXIII, and those to the right are from the tables given by Nichols and Howes on the pages indicated. Values in parentheses indicate that the corresponding band of the fluorescence spectrum is missing, or that it is not recorded by them. References are also missing for mercury uranyl acetate, sodium copper uranyl acetate, and rubidium uranyl nitrate, and they are therefore not included in the table.

TABLE XXXIV[1]—*Reversals of the uranyl bands*

Reversals by present method	Reversals observed by Nichols and Howes
Barium uranyl acetate	Pages 161, 167
Series D reverses at 1,830 and 2,085	E reverses at 2,009
F reverses at 2,018 and 2,100	
Potassium uranyl chloride	Pages 88–101
Series E reverses at 1,925	
G reverses at 1,943	
(H) reverses at (1,862) and (2,032)	
(I) reverses at (1,805), (1,888) and (1,975)	
Lithium uranyl acetate	Pages 158, 164
Series F reverses at 1,852 and 1,938	F′ at 2,105 reverses approximately with f′ at 2,109.
C reverses at 1,827	
D reverses at 2,005 and (1,924)	
Strontium uranyl acetate	Pages 160, 166
Series D reverses at 2,000	
H reverses at 2,050	
Uranyl acetate	Page 149
Series E reverses at 1,788	
F′ reverses at 1,803	
G reverses at 1,820, 1,988 and 2,075	
H reverses at 1,913 (2,088)	
B reverses at 1,860, 2,028	
E reverses at 1,965	
C′ reverses at 2,039	
F′ reverses at 2,053	

[1] Page numbers refer to Carnegie Inst. Wash. Pub. No. 298.

TABLE XXXIV—*Reversals of the uranyl bands*—Continued

Reversals by present method	Reversals observed by Nichols and Howes
Cæsium uranyl chloride	Pages 88–101
Series E_2'' reverses at (1,785), 1,868, 1,950, 2,032	B reverses at 1,974
B reverses at 1,812	C reverses at 1,993
C′ reverses at 1,828	D reverses at 2,005
D′ reverses at 1,845	E reverses at 2,026
D_2' reverses at 1,855	A reverses at 2,037
D reverses at 1,924	E_2' reverses at 2,030
A_2 reverses at 1,963	E_2'' reverses at 2,034
B_2 reverses at 1,985	
C_1 reverses at 1,998	
A_1 reverses at 1,787	B reverses at 1,969
C_1 reverses at 1,815	C reverses at 1,984
E_2' reverses at 1,943	D reverses at 2,004
C_2 reverses at 1,987	E reverses at 2,022
	A_2 reverses at 2,039
Potassium uranyl nitrate	Page 139
Series D reverses at 1,794	
I reverses at 1,824	
B reverses at 1,862	
E reverses at 1,976	
J reverses at 2,007	
F reverses at 2,069	
Cæsium uranyl sulphate	Pages 173, 178
Series E reverses at 1,795	F reverses at 2,061
G reverses at 1,815, (1,903)	
B reverses at 1,845	
C reverses at 1,864	
I reverses at 1,915	
D reverses at 1,952	
H reverses at 1,990	
F reverses at 2,063	
Rubidium uranyl sulphate	Pages 174, 178
Series I reverses at 1,810	E_1 reverses at 2,028
A′ reverses at (1,822), 1,907, 1,990	F reverses at 2,038
C reverses at 1,842, 2,012	G_1 reverses at 2,045
F reverses at 1,872, 1,957	
E reverses at 1,948	G reverses at 2,049

SUMMARY

Fluorescence is excited by wave-lengths of light between 0.550μ and 0.200μ, approximately. The intensity and range of excitation depends upon the substance.

There are three types of excitation observed:

1. Continuous, but variable in intensity, between 0.550 and 0.200μ.
2. Continuous, but variable in intensity, between 0.550 and 0.350μ.
3. Discontinuous, exhibiting a gap between 0.350 and 0.325μ, otherwise like type 1.

The range of the absorption spectra of twelve uranyl salts is extended to 0.550μ and to 0.320μ by the method herein discussed, a method which makes use of the fluorescence excited by dispersed ultra-

violet light, observing that wherever greater absorption takes place greater fluorescence results therefrom.

It is desirable to continue the work on the uranyl salts by this method, especially in the reversing region, because it is here that information can doubtless be obtained about the real mechanism of fluorescence.

The gap at 0.350 to 0.325μ in case of a few substances is noteworthy. No explanation is given, but further study of this type of excitation is desirable. It was observed that one of the uranyl compounds, namely, sodium uranyl cobalt acetate, appeared to the eye to give this type of excitation, but it was not studied photographically because of the relatively weak fluorescence produced.

V. NARROW FLUORESCENCE BANDS OF FLUORITES

[Describing experiments by Frances G. Wick]

Another important application of photography to fluorescence spectra was made by Miss Wick in her measurements of the narrow bands of certain fluorites. The following account is from her paper[1] entitled *A Spectroscopic Study of the Cathodo-Luminescence of Fluorite:*

"Fluorite crystals may be excited to luminescence, as is well known, by various forms of energy such as heat, light, ultra-violet radiations, cathode rays, X-rays, and radium. The luminescence due to cathode rays is characterized by a spectrum consisting of broad, diffuse bands upon which are superimposed, in the case of crystals from certain localities, sharp bands, some of which are nearly as narrow as lines of a gaseous spectrum. The source of these lines has been the subject of much investigation and some disagreement. Urbain[2] ascribed these lines to the presence of rare-earth impurities in quantities too small for detection by chemical analysis. Morse[3] was unable to prove that the lines observed were due to rare earths, but Tanaka[4] has identified certain rare earths as the active agents.

"The work here described was undertaken with the hope of getting further evidence as to the source of the sharp lines in the luminescence spectra of fluorites. The experimental difficulties involved in the study of the natural crystals are great, because the lines are very dim and the change of the surfaces of the crystals under cathode-ray bombardment makes necessary the exposure of a number of fresh surfaces for a single photograph. Since it is well known that heat treatment often has the effect of increasing the intensity of luminescence, it seemed possible that subjection of the fluorites to a high temperature before exposure to cathode rays might bring out the lines more strongly. The experiments here described show that by subjecting the fluorites to a temperature high enough to fuse them, very sharp line spectra of much greater intensity than any observed with the unheated specimens may be brought out, thus making visual and photo-

[1] Frances G. Wick. Physical Review (2), XXIV, p. 272, 1924.

[2] Urbain. Comptes Rendus 143, 825, 1906; Ann. de Chemie et de Phys. (8), 18, 256, 1909.

[3] Morse. Proc. Am. Acad., 41, 587, 1905-6; 43, 1, 1907-8.

[4] Tanaka. Jour. Opt. Soc. Am., 8, 501, 1924; also Chapter IV of this treatise.

graphic observations much easier. The results obtained from the study of such spectra verify the conclusion of Urbain that the lines in the luminescence spectra of fluorites are due to rare-earth impurities.

"From a large number of fluorites occurring in widely different localities and showing a great variety of colors and intensities of luminescence, a few were selected in which sharp, line-like bands were superimposed upon the characteristic broad bands of the cathode-ray spectra. Results are here given of observations upon the following varieties:

Specimen 1, blue-green fluorite from Weardale, England
Specimen 2, purple fluorite from Weardale, England
Specimen 3, yellow fluorite from Scoredale, England
Specimen 4, clear green fluorite from New South Wales
Specimen 5, chlorophane from Virginia Courthouse

"APPARATUS

"A part of the apparatus used for the study of the cathode-ray spectra is shown in figure 46. The crystal under observation was mounted in a tube, *T* (with a ground-glass joint, *B*) on an aluminum support so placed that the rays struck the specimen *C* at an angle of about 45 degrees. For the study of the ultra-violet spectra, the tube containing the specimen was made of Pyrex glass with a quartz window in front of the specimen *C*, and a Hilger quartz spectrograph was used. For the study of the visible spectra, a Hilger spectrograph or spectroscope of the constant-deviation type was placed with its collimator slit at *S*. The vacuum in the cathode-ray tube was maintained by an oil pump kept running continuously because the specimens gave off gas upon bombardment. A Wappler X-ray machine was used as a source of excitation, the voltage varying with the state of the vacuum up to a maximum measured by an equivalent spark-gap of a little over 2 cm. Ilford Special Rapid Panchromatic plates were used for work in the visible region and Seed 30 plates for work in the ultra-violet.

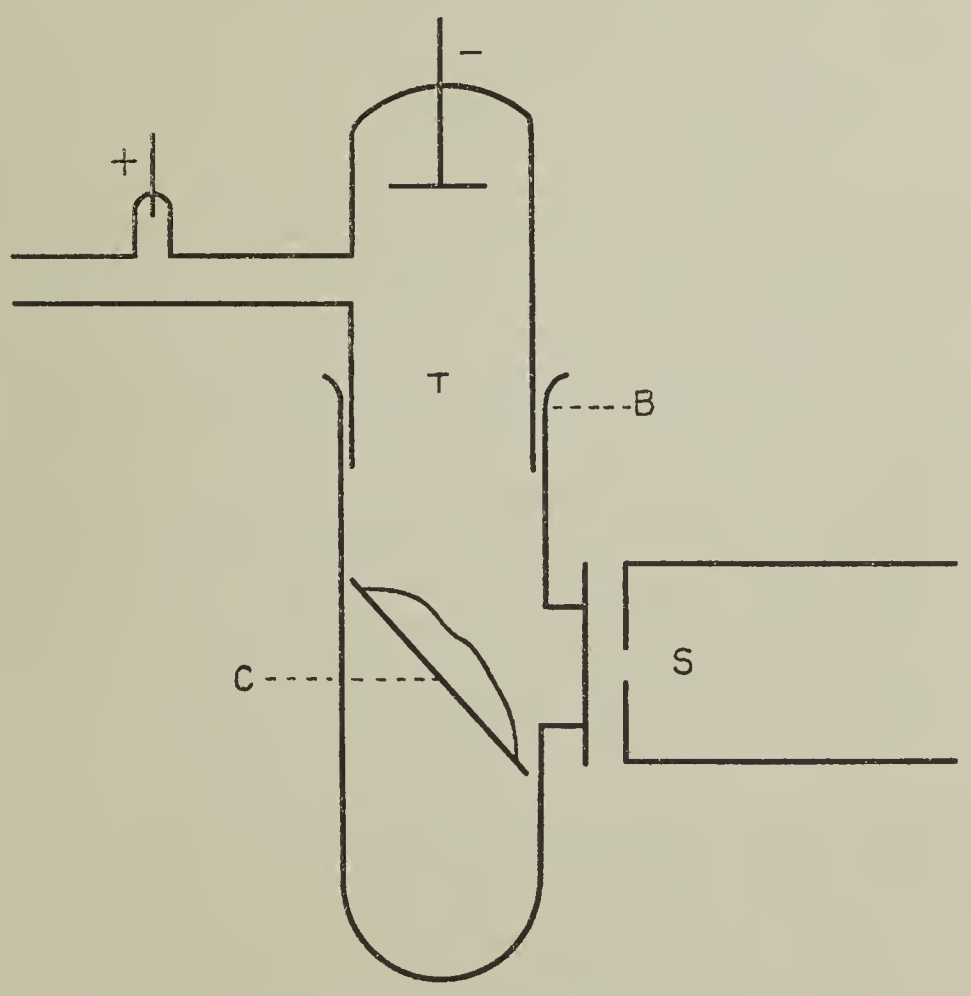


FIG. 46—Vacuum-tube

"EFFECT OF HEAT TREATMENT

"Specimens of fluorite were heated in an electric resistance furnace for periods of from one to three hours to temperatures varying from 300° to 600° C. Such treatment, as is well known, takes out all the natural color and usually causes the larger crystal masses to go to pieces or to become cracked and opaque. A study of the specimens under cathode-ray bom-

bardment shows that the luminescence very often has its color somewhat changed by this process of heating, so that the red end of the spectrum is more prominent than it was before, and, in general, the period of phosphorescence is lengthened. The intensity of the line-like bands is increased and that of the diffuse bands decreased by the heating, but the positions of the lines are not changed.

"Specimens of fluorite similar to those heated in the resistance furnace were heated by playing upon them an oxy-hydrogen or oxy-gas flame until fusion took place, at a temperature between 1100° and 1200° C. as indicated by an optical pyrometer. The cathodo-luminescence of the fused specimens was quite different from that of the unfused, often changing from blue or green to orange or red. The spectra are characterized by very sharp lines of much greater intensity, more numerous and most of them with different wave-lengths from those observed with the natural crystals.

"The character and intensity of the luminescence are greatly influenced by the conditions under which fusion takes place, such as the relative pressures of oxygen and hydrogen. It appears that the radical change brought about in the luminescence by fusion is due to the fact that, during the heating, a part of the calcium fluoride, at least a thin surface layer, is changed to calcium oxide, a conclusion verified by a chemical analysis kindly made by Dr. Kilpatrick, of the Department of Chemistry, Vassar College. In fact, by powdering the natural material and heating it in an ordinary air-gas blast until the surface becomes oxidized, exactly the same changes can be produced which are brought about by fusion. A very satisfactory way of preparing the material for study in the cathode-ray tube is to fuse the powdered fluorite in an oxy-gas flame and then to heat the surface further in an air-gas blast until more complete oxidation of the surface had taken place.

"From observations made upon these oxides, it appears that the relative intensities of lines and continuous bands depend upon the voltage applied to the tube, determined by the state of the vacuum, and upon the temperature of the specimen. In general, the lines come out most strongly and sharply at the high voltages, and the bands are most conspicuous at low voltages with higher current values. There is some evidence that the lines in the red end of the spectra are brought out by lower voltages than those of shorter wave-length and that raising the voltage applied to the tube pushes the continuous bands in the ultra-violet to shorter wave-lengths, but it is very difficult to tell just how much of the change is due to change in temperature under cathode-ray bombardment, and further experiments in which more accurate control of conditions is possible are necessary before any conclusions may be drawn.

"PHOTO-ELECTRIC MEASUREMENTS OF SPECTROGRAMS

"In order to get some quantitative idea of the changes in relative intensity of different parts of the spectra brought about by fusion, some of the photographs of the spectra obtained were measured by means of the photo-electric cell apparatus described in the preceding sections of this chapter. Samples of the curves obtained are shown in figure 47. Curve *A* was obtained from a natural specimen and shows a broad luminescence. Curve *B* shows the corresponding spectrum of the fused specimen and indicates that the intensity of the broad band is relatively greatly reduced, while numerous narrow bands appear. Figure 48 presents a small portion in full size of the actual record of such a run, in the case of a fused fluorite,

to show how by this method the successive galvanometer readings are plotted *directly* on cross-section paper instead of being put down in numerals. The series of dots thus formed becomes the actual record from the irregularities in which the more or less completely submerged components

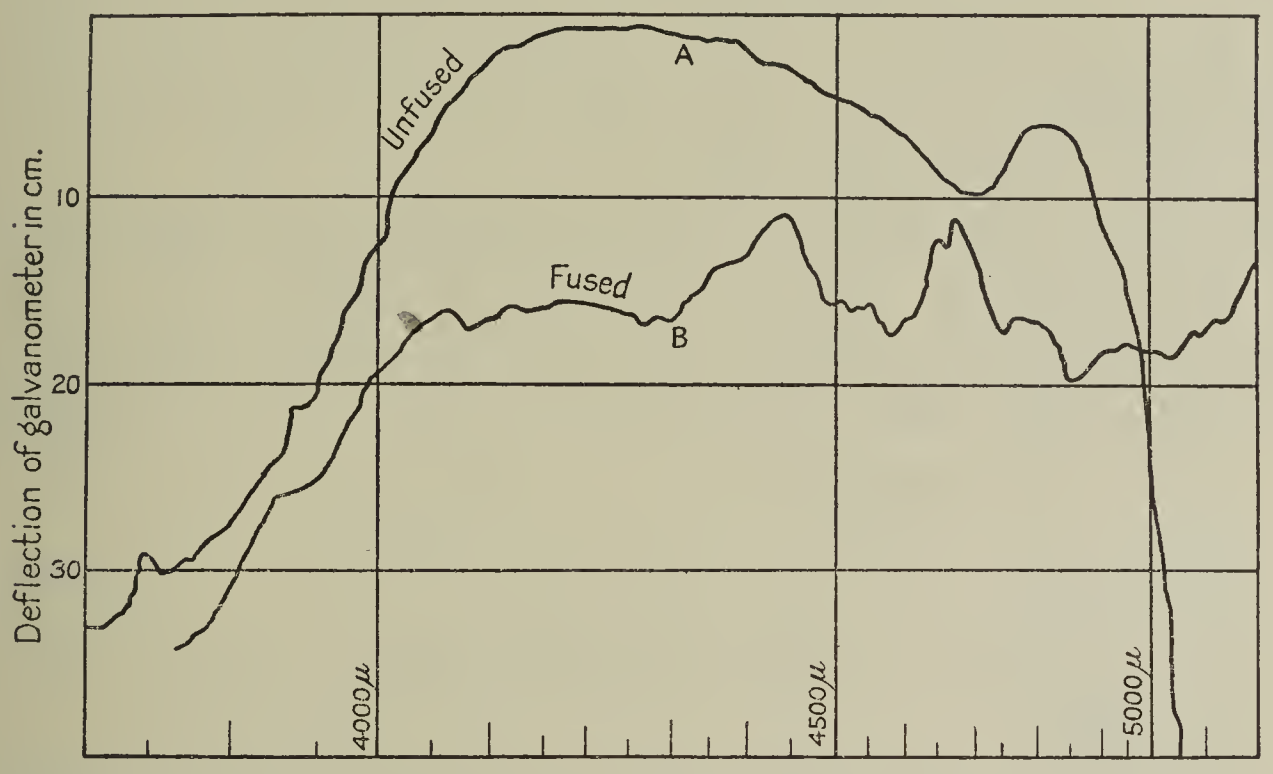


FIG. 47—Distribution of intensities in the fluorescence spectrum of unfused (*A*) and fused (*B*) fluorite

of the spectrum are located. To distinguish between accidental aberrations due to dust particles or optical defects in the film, etc., and variations caused by changes in the density of the negative itself, several runs are made, using different parts of the negative and also different photographs

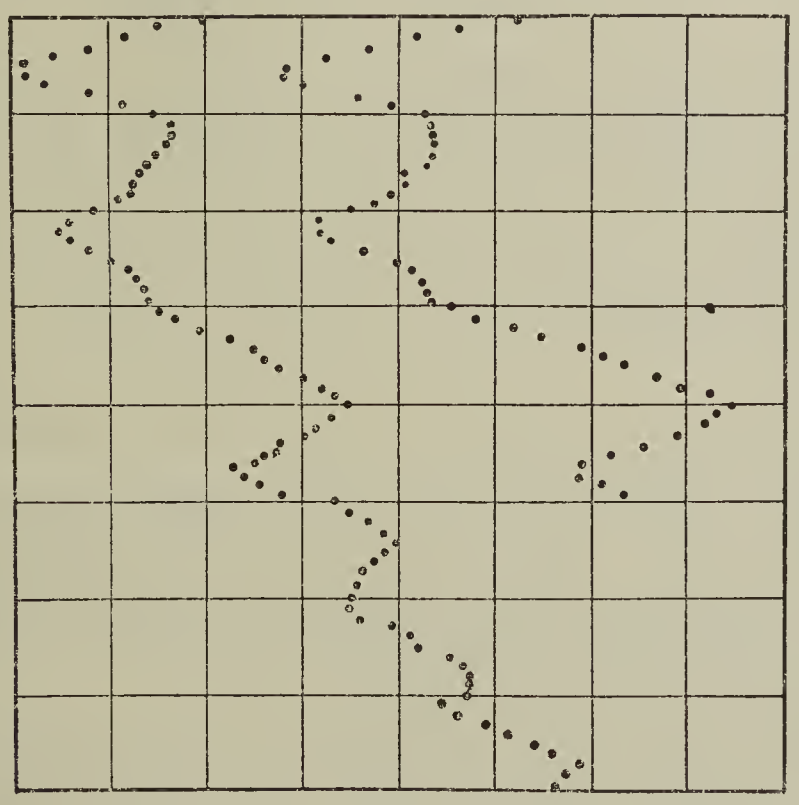


FIG. 48—Record of blackening of negative

of the same region in the spectrum, and only those crests and shoulders are counted which recur. Portions of a second run are shown in the upper part of the figure. In the small portion of a record here shown, which extends from about 0.4450μ to 0.4875μ, 80 readings appear. The distance apart of these in this part of the spectrum is therefore slightly more than 5 Ångströms

or approximately 2 wave-numbers. Each record for the entire spectrum band, of which several are required, will obviously contain several hundred readings.

"IDENTIFICATION OF LINES

"Urbain gives data with regard to the spectra obtained by placing very small amounts of various rare earths in calcium fluorite, calcium oxide, and calcium sulphate. The same rare earth produced a different spectrum in each of these different substances.

"In order to test for rare-earth impurities, specimen 1 was converted into calcium oxide by the method of heating described above, and some of the oxide was chemically converted into calcium sulphate. The spectra of these substances were observed visually and photographically and the results were compared with the spectra given by Urbain. The spectrum of the natural crystal (figure 49, spectrum 1) showed only a few lines, and

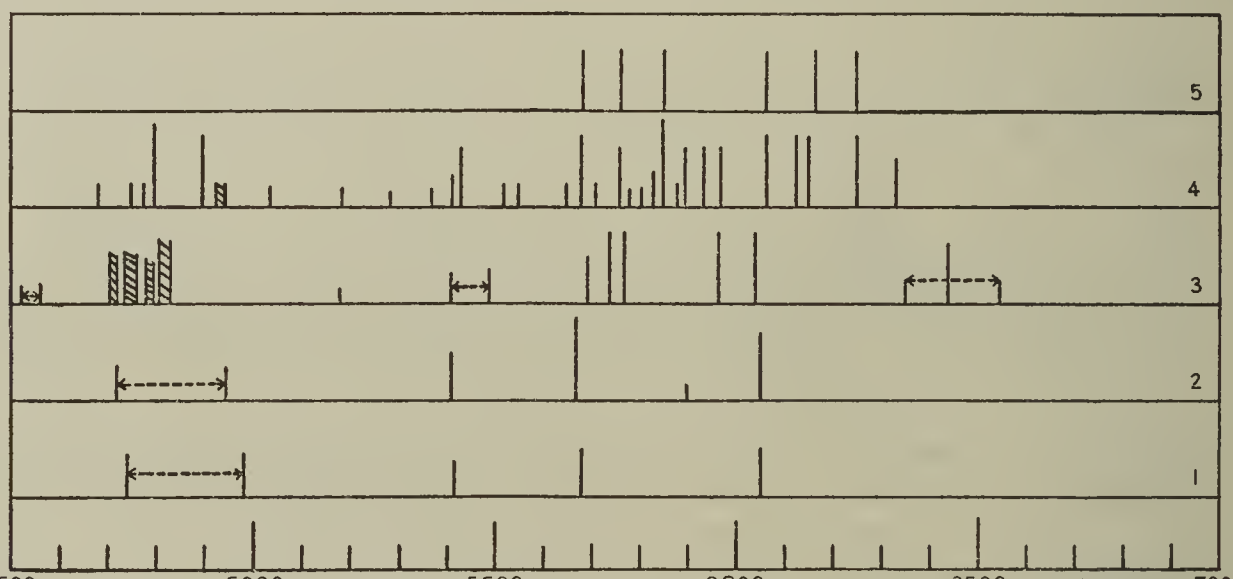


FIG. 49—Spectra of fluorite crystals

those were Urbain's strongest lines for samarium in calcium fluoride. The sulphate (figure 49, spectrum 3) showed a spectrum almost entirely due to dysprosium, and the oxide (figure 49, spectrum 4) gave a spectrum very rich in sharp, bright lines, the most conspicuous of which in the visible region were due to samarium. Dysprosium was also present, as shown especially by the strong citron band of Urbain, europium lines came out weakly, and terbium and gadolinium lines were very conspicuous in the ultra-violet.

"SPECTRA OF FUSED AND OXIDIZED SPECIMENS

"Since the lines in the fused and oxidized specimens are more numerous and are also very much brighter and more easily observed than those in the natural fluorites, the cathodo-luminescence spectra of the oxides prepared from different specimens were examined visually and photographically for the purpose of detecting rare-earth impurities.[1]

[1] In tables XXXV and XXXVI determinations by Miss Wick of wave-lengths longer than 6,500 were obtained from photographic plates. Where the fourth place is given as a subscript, Urbain's readings extended to three places only.

TABLE XXXV—*Visual observations of positions of narrow bands in the long wave-length end of the spectra of fused fluorites, and corresponding maxima of Urbain for rare earths in CaO.*

[*vs*, *s*, *m*, and *d* indicate relative intensities to be very strong, strong, medium, and dim; *h* indicates that the band is hazy or diffuse; all wave-lengths given in Å. U.]

Specimen of fluorite					Rare earths in CaO, data from Urbain
No. 1	No. 2	No. 3	No. 4	No. 5	
		6,763 *vvd*	6,759 *vd*		
6,740 *d, h*			6,754 *d*		*Dy* 675_0 *s* *Sm* 674_0 *m*
		6,675 *vvd*		6,670 *d*	*Dy* 667_0 *vd, h*
6,665 *m*					*Sm* 666_0 *m, h*
6,601 *m*					*Sm* 6,605 *s*
		6,612 *d*		6,617 *m*	
		6,572 *d*		6,568 *vd*	*Eu* 657_0 *vd, h*
6,556 *m*			6,550 *vd*	6,549 *m*	*Dy* 6,545 *vd* *Sm* 654_0 *m, h*
6,511 *m*					*Eu* 651_0 *d, h*
	6,522 *d, h*	6,521 *m*			
6,251 *s*	6,250 *vs*	6,253 *s*			*Sm* 6,265 *vs* *Eu* 6,245 *s*
6,156 *s*	6,159 *vd*	6,156 *m*		6,153 *s*	*Eu* 6,155 *m*
6,150 *s*			6,150 *vs*		*Sm* 6,150 *vs*
6,129 *s*	6,129 *vvs*	6,129 *s*			*Eu* 6,128 *vs*
6,063 *vd*	6,066 *vd*	6,063 *m*	6,062 *s*	6,071 *s*	*Pr* 6,065 *vs* *Sm* 6,052 *vs*
	6,045 *vvd*				*Pr* 6,045 *s*
5,971 *d*	5,974 *m*	5,979 *m*	5,977 *h*		*Eu* 597_0 *m*
5,931 *d*	5,932 *m*	5,935 *m*			*Eu* 593_0 *vs*
5,898 *d*	5,900 *s*	5,900 *m*			*Eu* 5,895 *ss* *Tb* 5,897 *vs*
5,876 *d*		5,878 *d*	5,880 *vd*		*Tb* 5,878 *s*
					Dy 5,877 *m, h*
5,851 *vvs*	5,851 *d*	5,850 *vvs*	5,850 *vvs*		*Dy* 5,848 *vvs*
				5,859 *m*	*Sm* 5,865 *d, h*
5,833 *d*	5,834 *vvd*	5,833 *vd*	5,829 *vd*		*Dy* 583_0 *vs*
5,805 *d*	5,808 *vvd*	5,805 *vd*	5,802 *vd*		*Dy* 5,805 *m*
5,783 *vd*	5,779 *vvd*	5,782 *vvd*	5,780 *vd*		*Dy* 5,785 *m*
					Dy 5,775 *m*
				5,764 *m*	*Sm* 5,762 *vs*
					Dy 5,763 *m*
5,756 *m, h*	5,757 *m*	5,757 *m, h*	5,756 *s*		*Dy* 5,752 *m*
	5,721 *vd*				*Sm* 5,725 ?
					Tb 5,717 *d*
5,714 *d*			5,712 *vd*		*Dy* 5,708 *vs*
5,683 *d*	5,683 *m, h*	5,686 *m, h*	5,684 *m*	5,681 *vd*	*Sm* 5,683 *vs*
5,650 *d, h*	5,645 *d, h*				*Eu* 5,645 *d*
5,551 *d, h*	5,548 *vvd*		5,549 *d, h*		*Tb* 5,550 *s, h*
					Eu 5,545 *d*
5,516 *d, h*	5,521 *d, h*		5,519 *d, h*		*Tb* 5,521 *s, h*
			5,497 *d, h*		*Tb* 5,495 *vs, h*
5,429 *m*			5,430 *s*		*Tb* 5,438 *s, h*
					Tb 5,425 *s, h*
5,411 *d, h*	5,412 *vvd*				*Tb* 540_0–539_0 max. of band
	5,401 *vvd*				*Eu* 5,401 *vs*
5,373 *vd*	5,371 *m, h*				*Eu* 5,365 *m*
	5,284 *vvd*				*Eu* 528_0 *m*
5,181 *vvd*					*Eu* 518_0 *m, h*
5,036 *vvd*			5,025 to 4,899	5,010 to 4,866	*Dy* 5,063–500_0 *d* *Dy* 495_0–491_0 *m, h* *Dy* 490_0–4,882 *s, h*

"Table XXXV gives visual observations of the five fused fluorites and the corresponding positions of crests recorded by Urbain in the cathode-ray luminescence of rare earths in calcium oxide. Figure 50 shows the same comparison graphically. The relative intensities of the narrow bands observed in specimens 1, 2, 4, and 5 are indicated by lines of different lengths, while the solid black diagrams given for comparison indicate the bands due to europium, samarium, and dysprosium in calcium oxide as represented by Urbain. The correspondence between the maxima of Urbain and the bands in the fused fluorites is very striking.

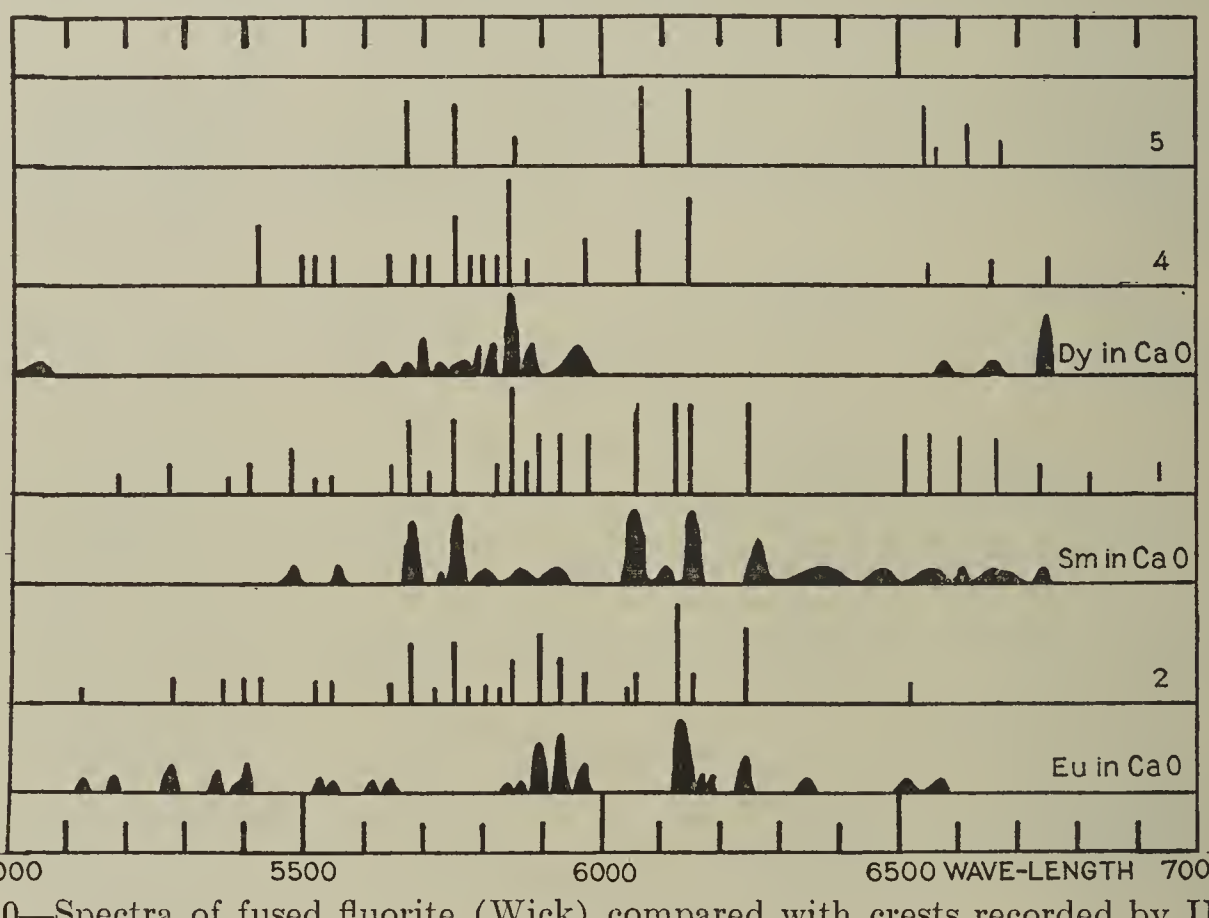


FIG. 50—Spectra of fused fluorite (Wick) compared with crests recorded by Urbain

"Table XXXVI gives a comparison of the positions of the bands in specimen 4 determined photographically, with the maxima of bands observed by Urbain in the spectra of rare earths in calcium oxide. It will be observed that the dysprosium, terbium, and gadolinium bands are very prominent in this specimen. The bands on the photographic plates were extremely sharp and narrow, many of them no wider than the lines of the cadmium spark used for comparison. They appear to be much narrower than those of Urbain.

"The spectroscopic observations on the various specimens lead to the following conclusions:

"*Specimen 1.* (Often occurring in good, clear crystals having a green transmission color and blue photo-luminescence, giving the material a blue-green appearance by daylight.) Spectrum lines from natural crystal principally due to samarium. The oxidized specimen shows strongest lines due to samarium and gadolinium. Terbium, dysprosium, and europium are also present.

"*Specimen 2.* (Sometimes occurring in clear, purple crystals, but more often in imperfect, purplish-white masses.) The strongest lines in the fused specimen are due to europium and the relative brightness of these lines indicates, according to Urbain,[1] the presence of a rela-

[1] Kayser. Spectroscopie, Vol. IV, p. 811.

tively large amount. Samarium, dysprosium, and gadolinium lines are also present, but these are much less prominent.

TABLE XXXVI—*Photographic observations of positions of narrow bands in the spectrum of fused fluorite No. 4 and corresponding maxima obtained by Urbain from rare earths in calcium oxide.*

Fluorite specimen 4	Rare earths in CaO, data from Urbain	Fluorite specimen 4	Rare earths in CaO, data from Urbain
5,683 *s*	*Dy* 569_0 *d, h*	4,336 *vvd*	*Eu* 433_0 *vs, h*
	Tb 5,687 to 5,602 *h*	4,328 *vvd*	*Eu* 4,315 *m*
5,654 *d*	*Dy* 566_0 to 563_0 *d, h*	4,307 *vd*	*Tb* 430_0 *vd, h*
5,560 *m*	*Tb* 5,570 middle of band	4,274 *vvd*	*Eu* 4,275 *m, h*
	Tb 5,550 *vs, h*	4,223 *m*	*Tb* 422_0 *m, n*
5,528 *m*	*Tb* 5,521 *vs, h*	4,213 *m*	*Tb* 421_0 *s, n*
5,506 *m*	*Tb* 5,508 *vs*	4,201 *m*	*Tb* 420_0 *vs*
5,437 *s*	*Tb* 5,438 *s, h*	4,193 *m*	*Tb* 419_0 *vs*
5,409 *vd*	*Tb* 540_0–539_0 max. of band	4,184 *m*	*Tb* 418_0 *s*
5,054 *vd*	*Dy* 5,063 to 500_0 *d, h*	4,168 *m*	*Tb* 416_0 *vs, h*
5,035 *vd*	*Dy* 503_0 *d, h*	4,151 *m, h*	
4,998 *d*		4,144 *m*	*Tb* 4,145 *m*
4,976 *d*		4,131 *m*	*Tb* 413_0 *vs*
4,946 *m*	*Dy* 4,955 to 491_0 *m*	4,121 *d*	*Tb* 412_0 *vs*
4,927 *d, h*		4,102 *d*	*Eu* 410_0 *d, h*
4,901 *s*	*Dy* 490_0 to 4,882	4,029 *d, h*	
	Dy 486_0 to 4,825	4,022 *d, h*	*Eu* 4,022 *vd, h*
4,850 *m, br, h*	*Tb* 4,855 *vs*	3,901 *d, h*	*Tb* 390_0 *vs, h*
4,832 *d*		3,879 *d, h*	*Tb* 3,880 *s, h*
4,825 *s*	*Tb* 4,825 *m, h*	3,806 *m*	*Tb* 3,805 *s, h*
4,800 *s*	*Dy* 4,797 *s, h*	3,800 *m*	
4,787 *vd*	*Tb* 4,785 to 4,730 *d, h*	3,794 *m*	*Tb* 3,795 to 378, *vs*, double
4,780 *m*		3,781 *m*	
4,767 *m*	*Dy* 477_0 *d*	3,575 *d*	
4,746 *d*	*Dy* 4,748 *m, h*	3,372.7 *d*	
4,719 *d*		3,165 *d*	*Gd* 3,166 beginning of band
4,685 *d, h, br*	*Dy* 469_0 to 4,665 *h*	3,158.2 *m*	*Gd* 3,158.5 *s*
4,646 *d*		3,155 *m*	*Gd* 3,155.5 *m*
4,624 *vd*	*Dy* 4,628 *h*	3,152.7 *s*	*Gd* 3,153.0 *s*
4,616 to 4,568	*Tb* 462_0 to 457_0 *m*	3,146.2 *vs*	*Gd* 3,147 *s, h*
		3,140.6 *s*	*Gd* 3,140.5 *s*
		3,135.3 *s*	*Gd* 3,134.0 *vs*
4,600 *d, h*	*Eu* 456_0 indistinct maximum	3,129.4 *d*	*Gd* 3,130 end of band
		3,122.3 *d*	
4,585 *d, h*		3,120.2 *s*	
4,545 *m*	*Dy* 454_0 *m, h*	3,119.2 *s*	
4,499 *m*	*Eu* 449_0 *vs, h*	3,114.9 *m*	*Gd* in CaF_2 3,120 *vs*; 3,118 *vs*; 3,115 *vs*; 3,113 *d*; 3,110 *d*
4,481 *m*		3,113.4 *d*	
4,472 *d*	*Tb* 4,472 *vs*	3,109.4 *d*	
	Eu 4,466 *vs, h*	3,093.2 *m*	*Gd* 3,094 *m, h*
4,457 *vd*	*Tb* 4,455 *vs*	3,087.7 *m*	*Gd* 3,088.5 *m, h*
4,440 *vd*	*Tb* 444_0 *m, h*	2,897.5	
4,430 *vd*		2,893	
4,408 *m*	*Tb* 441_0 *m, h*	2,828.1 *d*	*Gd* 2,828 *d*
4,393 *s*	*Tb* 4,395 *s*	2,797.3 *vd*	
4,378 *s*	*Tb* 437_0 *vs, h*	2,790.7 *vd*	*Gd* 2,789 *vd, h*
4,368 *s*	*Tb* 435_0 *s*	2,786.3 *vd*	
4,344 *s*	*Tb* 434_0 *d, h*		

"*Specimen 3.* (Found in clear, relatively good yellow crystals.) Spectrum of the oxide is similar to that of specimen 1, with a difference in the relative intensities of the lines. The strong "citron line" of dysprosium is by far the most conspicuous. Other lines show the presence of samarium, europium, gadolinium, and terbium.

"*Specimen 4.* (A clear, green specimen from a monozite-bearing lode in Torrington, New South Wales.) Natural specimen shows conspicuous bands indicating the presence of terbium, dysprosium, erbium, gadolinium, and samarium. In the fused specimen, lines characteristic of these elements, with the exception of erbium and with the addition of traces of europium, are present. The lines characteristic of gadolinium in calcium oxide and of gadolinium in calcium fluoride are present in the fused specimen, indicating that both the oxide and fluoride must be present in the fused specimen. The most conspicuous rare earth present is terbium.

"*Specimen 5.* (Material kindly furnished by the late Dr. Charles Baskerville; occurring in colorless and in brownish specimens.) The fused specimens show only a few lines in the visible, most of which are due to samarium. There is also evidence of dysprosium and europium. Lines in the ultra-violet due to gadolinium are weak. Specimen shows bright green thermo-luminescence at comparatively low temperatures.

"DISCUSSION OF RESULTS

"The presence of gadolinium is evident in all of the above specimens, as well as in all the other fluorites of which the spectra were photographed in the ultra-violet. The other most prevalent and conspicuous rare earths identified are samarium, europium, terbium, and dysprosium. Praseodymium appears to be present in some specimens. These results confirm the work of Urbain,[1] who detected gadolinium in all the fluorites he examined. In chlorophane (not from the same locality as that examined by the author) he found samarium, erbium, terbium, and dysprosium; in other specimens, terbium, praseodymium, samarium, and dysprosium. This work is also in agreement with the results of Tanaka,[2] (see Chapter IV), who, by an entirely different method, discovered the presence of samarium in samples of the same crystals as specimens 1 and 2 above.

It is of interest to note that the five most common rare earths which exist as impurities in fluorite have atomic weights which do not differ widely among themselves: Sm, 150.4; Eu, 152; Gd, 157.3; Tb, 159.2; Dy, 162.5. These elements all produce, in calcium oxide as diluent, lines which are narrower and sharper and more numerous than those which they produce in calcium fluorite. The extreme sharpness and relatively high intensity of some of the fluorescence bands in the fused fluorites at room temperature make further study of them a subject of considerable interest.

"While the process of fusion and subsequent heating changes the bombarded part of the specimen from calcium fluoride to calcium oxide, both the original fluoride and the resulting oxide are crystalline in form. Accord-

[1] Urbain. Ann. de Chemie et de Phys. (8), 18, 256 (1909).
[2] See Fluorspar, II and IV, notes on table XII (page 74).

ing to a suggestion made by Dr. E. C. Mendenhall, the sharpness of the lines in the luminescence spectra of substances containing minute quantities of rare earths may be explained if we assume that an atom of rare earth replaces an atom of the material used as diluent and forms an integral part of the regular crystal lattice of this material, for its position in the crystal structure would place upon its vibrations such limitations as to account for the sharpness of the lines in the spectrum of the light produced. This assumption may also explain why the luminescence spectrum of a given rare earth in one diluent, such as calcium fluoride, is radically different from that of the same earth in another diluent, such as calcium oxide,[1] for the limitations placed upon the vibrations by one crystal lattice are probably different from those imposed by another."

VI. MATHEMATICAL DETERMINATION OF SETS

For the picking out of the various sets in a spectrum containing numerous bands, the plan devised by Miss Mary A. Ewer has been found convenient. Her method is as follows:[2]

"The search for sets of constant frequency-interval in the spectra of various substances presents certain mathematical difficulties which are quite apt to be overlooked, no matter by what method one attacks the problem. There are, of course, two types of method possible—geometrical and arithmetical. One obvious arithmetic method is to group (by trial and error) the frequency numbers[3] into several sets, in each of which the difference between two neighboring frequency numbers is nearly divisible by the tentative frequency interval. This method would be satisfactory, were it not for the fact that the differences are always *nearly*, not *exactly*, divisible. When the range includes some 1,500 frequency-units, the little variations tend to have a cumulative effect, so that the difference between two numbers, one in the upper and one in the lower part of the set, becomes quite far from being divisible by the assumed frequency-interval.

"This difficulty may be overcome by the use of geometric methods. One of the best of these is as follows: The frequency numbers are laid out as abscissæ on a large sheet of cross-section paper, and from each point so determined a line is drawn parallel to the Y axis. A certain distance (usually that of the larger unit of the cross-section paper) along the Y axis is taken to represent I, the unknown frequency-interval. A ruler is now placed across the paper in such a direction that the line determined by its edge will have a positive slope, and its position and slope are varied until it crosses a number of the frequency lines at points representing multiples of I. Lines so crossed are assumed to represent members of the same set, and the frequency, or X-difference between two widely separated members, divided by the number of units of I, or y distance, between their junctions with the set-line, gives the value of I. An attempt is then made to group the remaining frequencies similarly, on lines parallel to the first one, that is, in sets having the same frequency-interval.

[1] E. C. Mendenhall. Science, 59, 219, 1924.

[2] Quoted with slight modifications from a report on a search for systematic relations in flame spectra (1922).

[3] Expressed in $1/\mu \times 10^3$.

"This method is not open to the objection that the supposed members of the set toward the farther end of the spectrum may fail to have the assumed relation to those in the near end. As much accuracy can be obtained in one part of the range as another. There is, however, a difficulty in this method also. Owing to the limits of accuracy in experiment, and also in drawing on cross-section paper, it is necessary to allow a slight variation above or below the crossing, just as, in the arithmetic method, it is necessary to accept *nearly* divisible in lieu of *exactly* divisible. Therefore, when four or more sets are mapped out, it would be very hard to find a frequency which would not fall upon one of them within the limits of reasonable accuracy. The same difficulty appears in another form when the frequency numbers are laid out as points along a straight line and the sets determined by means of stepping along the line with calipers. The essential nature of the trouble is that none of these methods show the relation of one series to another; that is, they do not show what, in the possible range of positions of spectral lines, would happen if a given line were in a different position than that in which it actually is. They do not show the actual mathematical structure, which is what we desire to know.

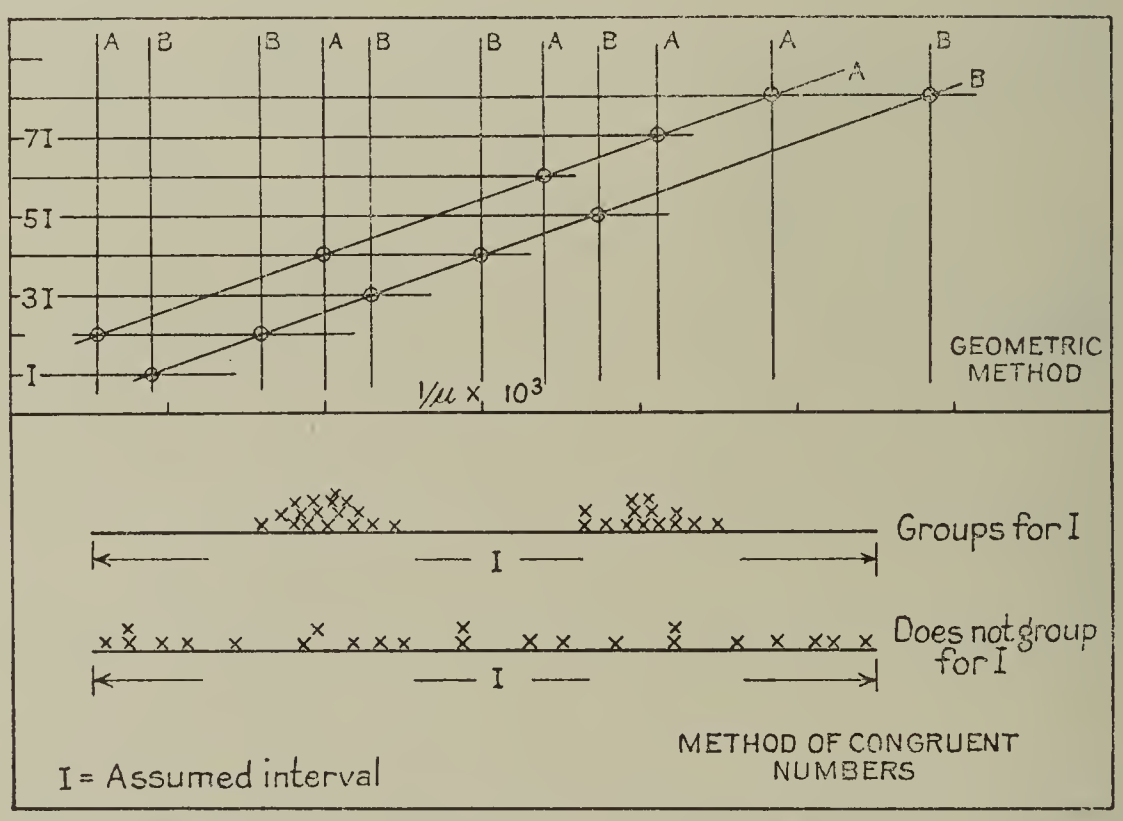


FIG. 51—Diagram illustrating two methods of search for constant-frequency interval

"There is one conceivable case in which one could tell at a glance the existence or non-existence of sets and their relation to one another; that is, if the assumed frequency-interval is exactly 10 (or exactly some multiple of 10). There could be no doubt about a set if the greater part of the frequencies were expressed by numbers ending in 7.0 and in 3.0 with all the rest ranging from 6.0 to 8.0 and from 2.0 to 4.0. There would then be two definite series having 10 as their interval and lying 4 units apart. But if the frequencies have all possible figures in units and tenths places, then 10 is not a possible interval. This may also be shown graphically by drawing a line 10 units long and locating each frequency on this line according to its units and tenths, say by a small x. If sets for 10 exist, these x's will occur in distinct groups; if not, they will be scattered all along the line, as shown in figure 51.

"This simple test for 10 as interval is based on the fact that our number system is such that it is possible to tell at a glance just how far after some multiple of 10 a given number comes, and, therefore, whether any two num-

bers come the same distance after a multiple of 10, *i. e.*, whether their difference is divisible by 10. A similar test may be made for any number whatsoever as interval, since the difference of two numbers is divisible by a third number, when the remainders after dividing the two numbers by the third are equal to each other. It is only necessary, therefore, to divide the frequencies to be studied by the assumed interval and make a table of the remainders.[1] Then the relation of the frequencies to that number as interval may be shown graphically by drawing a line whose length represents the interval and locating each remainder on this line by a small x. If sets exist, these x's will occur in distinct groups; if not, they will be scattered everywhere along the line.

"Moreover, it is often possible, in case the interval tested is not the true one, to tell whether a true interval is apt to lie in the immediate neighborhood. For if a number of the x's are scattered along the line in such a way that those representing higher frequencies are toward the upper part of the line, and those representing lower frequencies are toward the lower part, then a slightly larger value for the interval may make them fall into a group. If, however, those representing higher frequencies are toward the lower part of the line, a slightly smaller interval will be needed.

"The same thing may be shown, usually more easily than by dividing each frequency by the assumed interval, by beginning with a constant slightly lower than the lowest frequency of the spectrum one is studying, and, for each frequency, adding to this constant a multiple of the assumed interval such that the result will be less than that frequency by an amount smaller than the interval. The remainders are then plotted as has just been described. To express it mathematically, if I be the assumed interval, if F_1 be the lowest frequency in the data, if F_n be the nth frequency number in the data, if K be a constant such that $F_1 - K < I$, if r be a variable integer such that $F_n - (K + rI) < I$, and if we denote this expression $F_n - (K + rI)$ by the symbol R_n, then the method consists of plotting all values of R_n possible from the data, on a line of length I.

"If the values of R_n do not group for value I, but seem likely to do so for value $I' = I \pm d$, where d is a small amount, values of R'_n for I' can be obtained more easily than by repeating the original process, by means of the following general relation: $R'_n = R_n \mp rd$ ($\pm I$ if necessary), of which there are four possible cases: (1) where $I' = I + d$, and $rd < R_n$, then $R'_n = R_n - rd$; (2) where $I' = I + d$, and $rd > R_n$, then $R'_n = R_n + I - rd$; (3) where $I' = I - d$, and $R_n + rd < I'$, then $R'_n = R_n + rd$; (4) where $I' = I - d$, and $R_n + rd > I'$, then $R'_n = R_n + rd - I'$.

"The application of this method is fairly rapid when one knows the general location of the interval, and when the range and number of frequency values is not too great. If the range is as great as 1,500 units, the difference between taking $I = 15$ and $I' = 15.1$ amounts to 10 units at the upper end of the scale, an effect analogous to that produced on the moving end of a long line whose slope is changed very slightly, keeping one end of the line fixed. Again, if the number of frequency values is very high, the method becomes exceedingly tedious and the results extremely difficult to judge. The limitations of this method, therefore, are that with it alone one can not explore the entire range of possible numbers in the search for frequency intervals, and that it becomes unwieldy in the case of a very rich and long spectrum. Its usefulness is confined to cases where we have reason to suspect that a frequency-interval lies in a certain definite neighborhood; and

[1] The method is, of course, no more than an application to the problem of the theory of *congruent numbers*.

especially in cases where a certain frequency-interval seems to be a true one and it is desirable to test it to see whether sets based on it are actual or only apparent.

VII. A CRITICAL STUDY OF FREQUENCY-INTERVALS

[Experiments by R. M. Fisher.]

Shortly after the completion of the work of Tanaka described in Chapters III and IV, the remarkable relation discovered by him between the atomic weight of an activator and the frequency interval of the fluorescence spectrum produced through its agency, was put to a critical test. This investigation was born of a healthy scepticism concerning the reality of spectral structures invisible to the eye and only revealed as the indirect product of spectro-photometric measurements. It was carried out by Mr. R. M. Fisher in a manner intended to be conclusive, and to that end was so planned as to be as far as possible independent of the visual method. His results, which have not yet been published, are given in slightly abridged form in the following paragraphs:

"The general course of a typical experiment was as follows: The solid solution was prepared, bombarded by cathode rays, and thus caused to emit fluorescent light. The spectrum was photographed and a record of the density throughout the spectrum obtained by means of a recording densitometer. A number of such records were taken for each substance and were then examined and compared for evidence of the existence of bands in the spectrum. Complete data for a solution was in the form of a table of wave numbers, each corresponding to the crest of a component band. The data were then analyzed to determine, first, whether there existed constant-frequency interval sets with more members present than were to be expected from a random distribution, and secondly, whether the intervals of such sets agreed with those found by Tanaka.

"No attempt was made to duplicate Tanaka's experiments in any exact way, both because the solutions which he used were not available, and because the wave-length range best adapted for visual measurements can not be photographed without prolonged exposures, which were not thought to be desirable. The same metallic activators as used by Tanaka were employed, the spectra obtained by cathodo-excitation.

MATERIALS TESTED

The fluorescent materials used and their method of preparation were as follows:

"1. *Columbium*—The solid solution of columbium was prepared by W. S. Andrews, of the General Electric Company, and given to the writer by Dr. E. L. Nichols. It was described by the maker as 'synthetic willemite—zinc silicate with a trace of Cb_2O_5, heated to about 1000 C. for 15 minutes.' The powder is stable, retaining its fluorescent properties when exposed to air.

"2. *Manganese*—To 1 gram of $CaCO_3$ (Kahlbaum) was added 1 c. c. of N/100 solution of $MnCl_2$. The mixture was then heated in a crucible to a

cherry red, this temperature being maintained for 15 minutes. This material soon lost its fluorescent properties on exposure to air, and had to be used at once.

"3. *Copper*—1.545 grams of $CuCl_2 2H_2O$ were dissolved in 100 c. c. of water. 1 c. c. of this solution was diluted with 500 c. c. of water. 1.5 c. c. of this were put into the crucible with 1 gram of $CaCO_3$ and the mixture calcined for 15 minutes. This gave an extremely small trace of copper, 3 molecules of copper to 100,000 molecules of CaO.

"4. *Lenard and Klatt Copper*—This preparation was one of the standard Lenard and Klatt sulphides, No. 32, marked Ca, Cu, Li_2SO_4.

"5. *Kahlbaum's* $CaCO_3$, which had been used as a base as indicated above was calcined for 15 minutes and used without known activator.

"Excitation of Fluorescence

"Fluorescence was produced by bombarding the specimen with electrons. The material, finely powdered, was spread upon an aluminum plate, and the plate then mounted inside a glass tube, the plate making an angle of 45° with the side of the tube. The tube was then joined to a vacuum system having two sealed-in electrodes, so arranged that the cathode was vertically above the specimen. Fluorescence of the glass walls of the tube was prevented by shielding them with aluminum, an aperture being left for the escape of light from the specimen. (See figure 46, page 131.) A potential difference of 4,000 to 5,000 volts was usually sufficient to cause the discharge to pass and to produce brilliant fluorescence in the specimen thus bombarded. The optimum conditions for most intense fluorescence were obtained by varying the vacuum within such limits as is possible when using a Central Scientific Company 'Hivac' pump, and were usually found at about the lowest pressure which that pump is capable of producing.

"A spectrograph of the Hilger constant-deviation type was used. The slit was placed as close as possible to the fluorescent specimen, so that light from the specimen filled the slit. The slit-width used was always 0.00125 cm., chosen empirically, but in approximate agreement with Schuster's value for maximum brightness and resolution. Three kinds of plates, Eastman Orthonon, Eastman Polychrome, and Wratten and Wainright Panchromatic, were used for each substance studied, and on each kind of plate a series of exposures was made, usually in the following order: 5 seconds, 10 seconds, 15 seconds . . . 60 seconds. The plates were all developed for 4 minutes, at 70° F., using Eastman M. Q. developer and fixed in Eastman acid hypo. Development and fixing were done in complete darkness to prevent fogging.

"Density Record

"The spectrum photograph, for each substance used, was a continuous band and, so far as the eye could detect, this band was uniformly varying without any sharply defined bands or lines. A photo-electric densitometer, similar to that described by Perrine,[1] showed, however, that irregularities did exist.

"Each record of the densitometer was a graph of galvanometer deflection plotted against distance from some known position in the fluorescence spectrum. The significant part of this record was the presence of small irregularities or ripples on the curve. Ripples might mean real intensity differ-

[1] Physical Review, 22, 1923, p. 48. See also figure 27, page 89.

ences in the spectrum or they might be caused by some peculiarity in the apparatus used for recording. They might, for example, be caused by diffraction bands.

"But if diffraction bands are present, they should be the same on the photographs of different spectra. A comparison of the bands found for different activators, *e. g.*, columbium and copper, shows no agreement. Ripples might be caused also by mechanical disturbance. As a test of freedom from such disturbances, a run was made lasting for one and one-half hours, exactly like the regular record runs, except that there was no plate in the densitometer. The resulting graph showed only one or two very small disturbances, none large enough to be counted on a record of an actual spectrum.

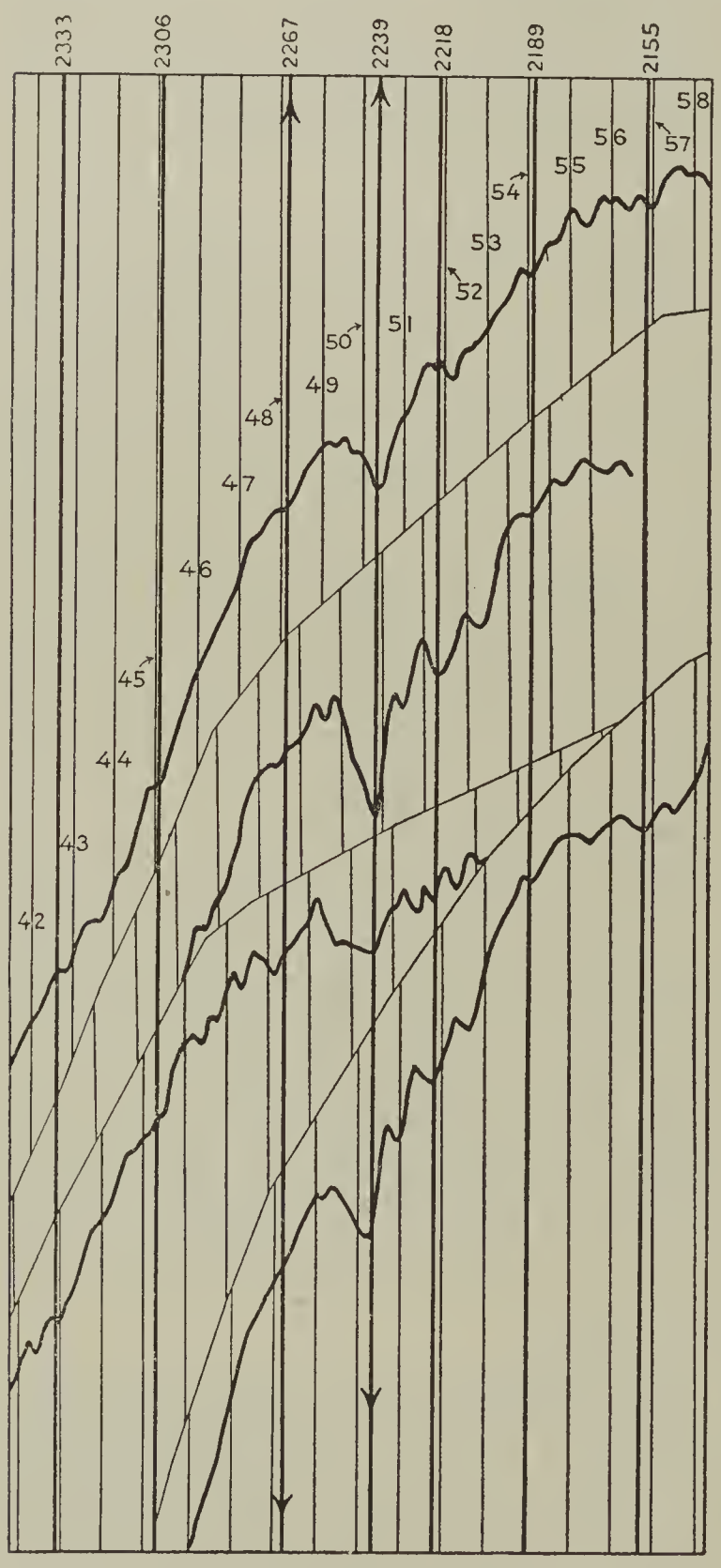


FIG. 52—Enlarged portion of the copper records mounted together, showing agreement and the corresponding wave-numbers. Only 4 of the 6 records are shown.

"SELECTION OF THE BANDS

"The density record of each plate showed a large number of bands, as many as 50 on the average in the case of columbium, and for this substance 9 plates were analyzed. To find agreements among the plates, the data for one were plotted along a horizontal line, those for the second on a parallel line above the first, and so on, the complete plot consisting of nine horizontal rows of points.

"Ideally, an agreement would be indicated on this plot by nine points, one above the other in a vertical line. Actually, since an error of two wave-numbers was to be expected in locating a crest, the points should be scattered within a rectangle 4 units wide. Also, since the plates were exposed for different times, one could not expect a band to show on every plate. What was sought, therefore, was a tendency to vertical grouping within the limits mentioned.

"In order to have some definite way of specifying the method of selection, the following criterion was developed. Suppose that a number of points equal to that actually plotted were scattered upon the paper at random: How many might one expect to find in a rectangle 4 units wide? The proper degree of expectation is indicated by the probability of such a happening, and the

significance of what one does actually find depends on the smallness of its probability.

"The criterion for an agreement between plates was arbitrarily taken to be the finding of a group of points within an interval of 4 cm. or less, having a probability of less than 0.04. Under the conditions of these experiments this criterion required that a band must appear on six of the nine plates in order to be accepted as real.

"Search for Set Relations

"There resulted from the foregoing analysis a table of wave-numbers for each substance. Set relations among the members of each table were sought by a method similar to that of Miss Ewer described in the foregoing section of this chapter. The method actually used was suggested to the writer by Mr. D. T. Wilber, Carnegie Research Assistant at Cornell University.

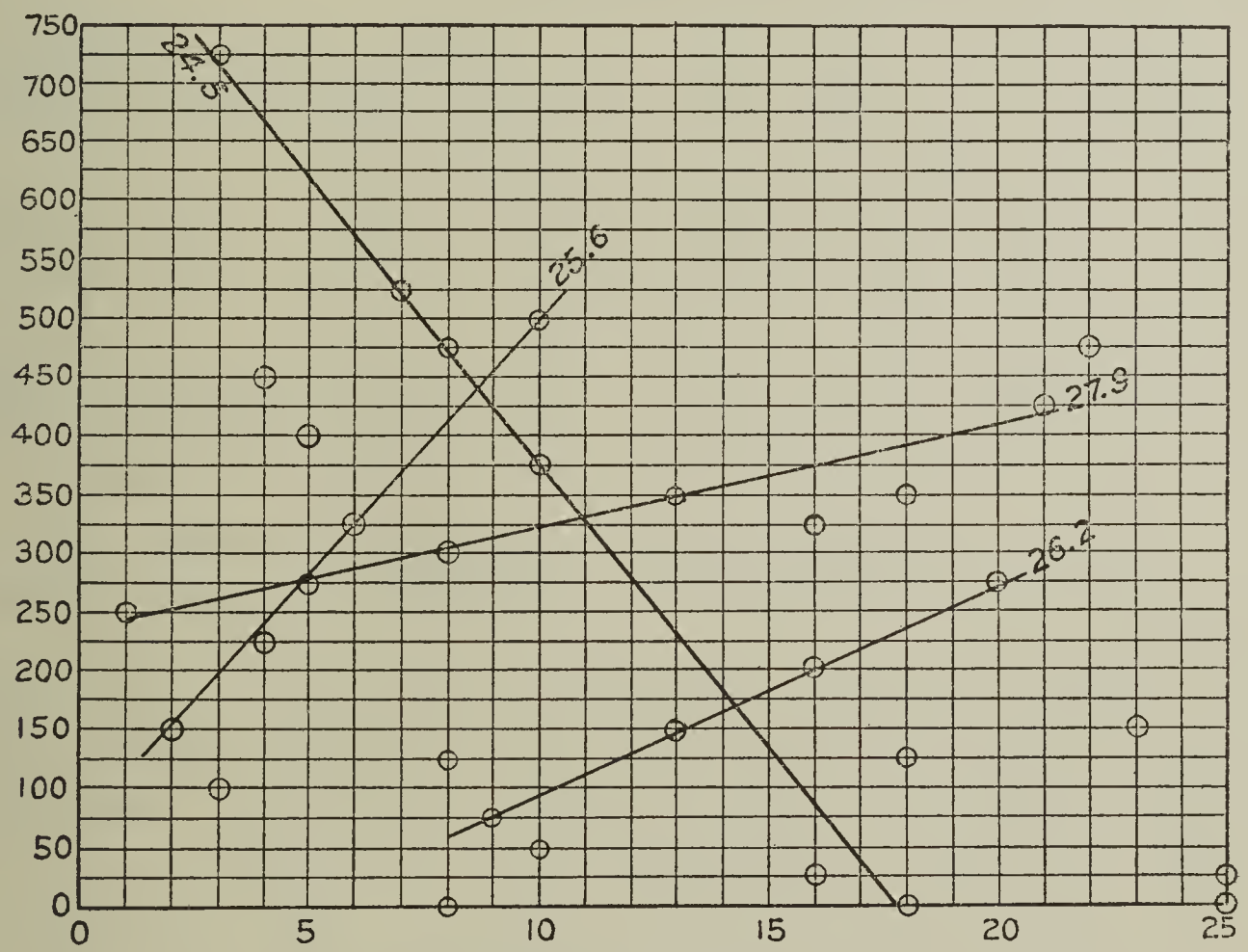


Fig. 53—Graphical method of search for sets of constant frequency-interval as used by Fisher

"For convenience, the wave-numbers of a table were each subtracted from the largest member, giving a table of differences. These were tested for constant-difference sets in the following way: Suppose it were desired to test for intervals near 20. On squared paper X and Y axes were chosen. The X axis was then numbered from zero to 20, and any members of the difference table between 0 and 20 plotted on this axis in appropriate positions. Any members between 20 and 40 were plotted similarly on the next line above, between 40 and 60 on the next, and so on until the whole table had been plotted.

"All points lying on the same vertical line (parallel to the Y axis) were members of a set having the interval 20. Members of a set whose interval was 19 would be found on a line tilted to the left and making an angle of 45° with the Y axis. Sets whose interval lay between 19 and 20 were indicated by points in lines inclined to the left at some angle between 0 and 45°. Similarly, points lying along a line inclined to the right at 45° were members of a set of interval 21. (See fig. 53.)

"By this method, all frequency intervals between 17 and 23 could be tested not only for integral values but all values. The sets so found were always checked by use of an adding machine.

"This process was repeated for the values 25, 30, 35, and 40. Any sets whose interval was greater than 40 could easily be detected without further plotting, since its interval would be some integral number of times greater than a value already tested. For example, any terms of a set whose interval was 42 would already be represented in the series of interval 21.

"Probability Criteria

"In no case was an entire set found; always, rather, a few scattered terms. For instance, in the case of columbium, 7 members out of a possible 21 were found in the set whose interval was 33.7. The 7 were not consecutive, but scattered throughout the range.

"It is natural to question whether the finding of so few terms is of any significance; whether as many might not appear if random data were analyzed in the same way. The only definite way of answering this is to calculate the probability of such an occurrence, assuming the data to be distributed at random. The problem may be stated in this way:

"Given a range of N consecutive numbers, and let n of these be chosen at random. What is the probability that r of those chosen are members of a constant-difference series whose interval is j?

"The value N corresponds to the range of wave-numbers represented in the spectrum under investigation, n is the number of agreements found on analyzing the different photographs of this spectrum, r the number of series members actually found, and j the interval of the series in question."

An expression was found for the probability as dependent on N, n, r, and j,[1] and was used to compute the probabilities given in the tables that follow.

In analyzing the data, probability of the order of magnitude of 0.001 or less was chosen as criterion for the significance of a set. A test of the method used, when applied to random data, was made by applying it to a list of thirty numbers chosen as follows:

In the Physico-Chemical Tables,[2] volume 1, page 45, table VIII, there is a list of the hyperbolic logarithms of prime numbers, computed to twelve decimal places. Beginning at a place in the table chosen at random, the last three figures of the logarithm were copied. This was repeated for the next twenty-nine logarithms whose last three figures were below 700. These numbers were arranged in ascending order, and analyzed by the method described, for the existence of sets having intervals from 15 to 40. The lowest probability of any set thus found was 0.025.

[1] The formula and its derivation are given in full in Dr. Fisher's manuscript thesis, in the Cornell University library.

[2] J. Castell-Evans, London, 1902.

RESULTS

A. Columbium in Zinc Silicate

$1/\mu \times 10^3$ (letters indicate sets to which the band bears relation)

2046	2187 ABD	2252 D	2316	2500	2656 CD
2078 B	2199	2260 A	2323 B	2556 D	2678
2092	2203 C	2268 BC	2340	2601 A	2700 A
2118 D	2211 A	2285 AD	2355	2635	2720 C
2133 B	2236 AC	2300 C	2430 ABC	2646	2730 B
2151 D					

Sets with probabilities less than 0.002 (1) (2)

Set A. Interval 24.4 Prob. 0.00017		Set B. Interval 27.2 Prob. 0.0015		Set C. Interval 32.3 Prob. 0.0003		Set D. Interval 33.7 Prob. 0.0002	
2,187	0	2,078	0	2,203	0	2,118	0
2,211	−0.4	2,133	−0.6	2,236	0.7	2,151	−0.7
2,236	0.2	2,187	0.2	2,268	0.4	2,187	1.6
2,260	−0.2	2,268	−0.4	2,300	0.1	2,252	0.8
2,285	0.4	2,323	0.2	2,430	0.9	2,285	−1.5
2,430	−1.0	2,430	−1.6	2,656	0.8	2,556	−0.1
2,601	−0.8	2,530	−0.8	2,720	0.2	2,656	−1.2
2,700	−0.6						

B. Manganese in Calcium Oxide

$1/\mu \times 10^3$ (letters indicate sets to which the band bears relation)

1928	2204	2447 A	2594 BC	2650	2700 A
2059 C	2307 AC	2493 B	2602	2662 B	2710
2117 B	2344	2531 A	2634 C	2666	2720
2184 BC	2390 AB	2540	2642 A	2686	2723

Sets with probabilities less than 0.008 (1)

Set A. Interval 28. Probability 0.0025		Set B. Interval 34. Probability 0.00076		Set C. Interval 41. Probability 0.007	
2,307	0	2,117	0	2,059	−2.0
2,390	−1.0	2,184	−1.0	2,184	0
2,447	0	2,390	1.0	2,307	0
2,531	0	2,493	2.0	2,594	0
2,642	−1.0	2,594	1.0	2,634	−1.0
2,700	1.0	2,662	1.0		

(1) No other sets were found having probabilities less than 0.01, between intervals 15 and 45.

(2) Two sets were found with probability greater than 0.01: one of 5 members, interval 37.7, probability 0.01; the other of 4 members, interval 39.7, probability 0.1.

C. Copper in Calcium Oxide

$1/\mu \times 10^3$ (letters indicate sets to which the band bears relation)					
2000 B	2239	2362	2515 A	2594	2676
2083	2267	2384 A	2535	2611	2683
2097	2287 A	2416 A	2541 B	2622	2695 B
2116 B	2306	2442	2548 A	2632	2712 A
2155 AB	2333	2472	2562	2657 B	2716
2189 A	2351 A	2503 B	2574	2674	2727
2218					

Sets with probabilities less than 0.0004(1)(2)

Set A. Interval 32.7. Probability 0.000009				Set B. Interval 38.5. Probability 0.00038			
2,155	0.3	2,416	1.0	2,000	−2.0	2,541	0
2,189	−1.0	2,515	0	2,116	1.5	2,657	−0.5
2,287	−0.9	2,548	0	2,155	−1.0	2,695	0
2,351	0.5	2,712	0	2,503	0.5		
2,384	1.0						

D. Lenard and Klatt Copper (Ca, Cu, Li_2SO_4)

$1/\mu \times 10^3$ (letters indicate sets to which the band bears relation)					
1865 A	2154	2267 A	2379 B	2465 B	2558
1880	2162 AB	2277	2392 A	2472	2567
1920	2203 A	2300	2414 A	2475	2583 A
2076 AB	2223 A	2314 B	2435 A	2505	2590
2098 AB	2240	2328 A	2445	2524	2600
2111	2245 A	2357 B	2456 A	2548	2608
2125					

Sets with probabilities less than 0.002 (1)(3)

Set A.(4) Interval 21.1. Probability 10^{-8}				Set B. Interval 21.6. Probability 0.001	
1,865	−0.6	2,267	0.5	2,076	0.2
2,076	−0.6	2,328	−1.8	2,098	−0.2
2,098	0.3	2,392	0.9	2,162	0.6
2,162	1.0	2,414	0.2	2,314	−0.2
2,203	−0.2	2,435	−0.3	2,357	0
2,223	1.3	2,456	0.4	2,379	0.4
2,245	0.4	2,583	0	2,465	0

(1) No other sets were found having probabilities less than 0.01, between intervals 15 and 45.

(2) Sets with probabilities greater than 0.01 were found with intervals 19, 21, 28, 36.3, 38.8.

(3) Six-member sets with probabilities greater than 0.01 were found with intervals 20 and 27.9; five-member sets with intervals 21.3, 35, 41.3, and 41.7 respectively.

(4) This set also contains 9 members of a set whose interval is twice 21.1, 7 members for three times this interval, 6 members for interval 84.4, 4 members for interval 105.5 and 5 members for interval 126.6.

E. Calcium Oxide

(No known activator. Cu and Mn probably present in very minute amounts)

$1/\mu \times 10^3$ (letters indicate sets to which the band bears relation)

1902 BCFG	2106 BF	2266 DJ	2412 F	2539 EH	2656 DH
1945 ABCEH	2120 EG	2286	2426 G	2550 DGJ	2668 J
1971 F	2144	2315 B	2440 B	2586 DH	2692 ADJ
2005 FJ	2161 D	2334 G	2480 BDFJ	2594	2704 G
2025 BCG	2176	2354 BC	2490 H	2612 G	2715 EJ
2035	2190 BCE	2360 AJ	2503 J	2633 H	2723 C
2051 EJ	2218 J	2372 DH	2515 DFH	2641 C	2726
2070 A	2227	2400 AE	2527 AJ	2645 BEJ	2734
	2242 FGJ				

Sets with probabilities less than 0.002[1][2]

Set A. Interval 41.5. Probability 0.001		Set B. Interval 41.3. Probability 0.00001				Set C. Interval 41. Probability 0.0001	
1,945	0	1,902	0.4	2,315	0.4	1,902	1.0
2,070	0.5	(1,945)	2.0	2,354	1.9	1,945	1.0
2,360	0	2,025	−0.5	2,440	1.3	2,025	1.0
2,400	−1.5	2,106	−1.1	2,480	0	2,190	0
2,527	1.0	2,190	−0.7	2,645	0	2,354	0
2,692	0					2,641	0
						2,723	0

Set D. Interval 35.4. Probability 0.0001		Set E. Interval 35. Probability 0.001.		Set F. Interval 34. Probability 0.001.		Set G. Interval 30.8. Probability 0.00001.	
2,161	0	1,945	0	1,902	0	1,902	1.2
2,266	−1.2	2,051	−1.0	1,971	−1.0	2,025	1.4
2,372	−1.4	2,120	0	2,005	−1.0	2,120	1.2
2,480	0	2,190	0	2,106	0	2,242	0
2,515	0	2,400	0	2,242	0	2,334	−0.4
2,550	−0.4	2,539	1.0	2,412	0	2,426	−0.8
2,586	0.2	2,645	0	2,480	0	2,550	0
2,656	−0.6	2,715	0	2,515	1.0	2,612	0.6
2,692	0					2,704	0

Set H. Interval 23.7. Probability 10^{-8}.				Set J. Interval 23.7. Probability 10^{-8}.			
1,945	−0.7	2,586	−0.4	2,005	0	2,503	0.3
2,372	−0.3	2,633	0	2,051	−0.4	2,527	0.6
2,490	0.8	2,656	−0.7	2,218	−1.0	2,550	0.2
2,515	0.5			2,242	0	2,645	1.0
2,539	0.8			2,266	0.3	2,668	−0.6
				2,360	−0.5	2,692	−0.3
				2,480	1.0	2,715	0

(1) No other sets were found having probabilities less than 0.01, between intervals 15 and 45.

(2) Two sets were found with probability greater than 0.01: one of 8 members, interval 20.8; the other of 7 members, interval 26.

SUMMARY

Columbium

Intervals (prob. less than 0.002)	24.4	27.2	32.3	33.7	
Intervals (prob. greater than 0.01)	37.7	39.7			
Tanaka intervals	21.5	25.5			

Manganese

Intervals (prob. less than 0.008)	28.0	34.0	41.0		
Intervals (prob. greater than 0.01)	25.8 two series				
Tanaka intervals	34.0	42.0			

Copper (in Calcium Oxide)

Intervals (prob. less than 0.0004)	32.7	38.5			
Intervals (prob. greater than 0.01)	19.0	21.0	28.0	36.3	38.8
Tanaka intervals	34.0				

Copper (Lenard and Klatt)

Intervals (prob. less than 0.002)	21.1	21.6				
Intervals (prob. greater than 0.01)	20.0	21.3	29.9	35.0	41.3	41.7
Tanaka interval	34.0					

Calcium Oxide (no known activator)

Intervals (prob. less than 0.002)	23.7	30.8	34.0	35.0	35.4	41.0
	41.3	41.5	42.0			
Intervals (prob. greater than 0.01)	20.8	26.0				

"CONCLUSIONS

"Of the two questions proposed in the beginning of this report, the first may be answered: The results show the existence of what have been called 'partially submerged' series in the spectra of all the fluorescent substances tested. Although the series are incomplete, probability considerations show that many more members are present than could be expected if the data were random in its distribution.

"As to the relation between interval and activator, the outcome is not so clear. In the case of columbium, one of the Tanaka intervals is somewhere near one of those found by the writer, the other was not found.

"For magnesium the check is very close, for copper agreement is fairly close in the case of one solution, but the other has no interval near that of Tanaka among the series of small probability.

"The final data on calcium oxide without known activator is significant in this connection, because it clearly shows the impossibility of specifying what activator it is that is producing the fluorescence. Indeed, it seems probable that there are traces of several, perhaps many, impurities, in amounts too small to be detected by chemical tests, but in concentration highly favorable to fluorescence. This powder, the purest obtainable, gave the most brilliant fluorescence of any of those tried. Two probable impurities are copper and manganese, and if these are assumed to be present, the grouping of three intervals near 35 and three intervals between 41 and 42 becomes significant, since the Tanaka intervals for copper and manganese are respectively 34 and 42."

CHAPTER VI

STUDIES OF CERTAIN ACTIVATORS

I. URANIUM AS AN ACTIVATOR

[Describing experiments of E. L. Nichols and Mabel K. Slattery.]

In luminescence, uranium is chiefly known as a component of the uranyl salts, all or nearly all of which are strongly fluorescent alike in the crystalline form and in aqueous solution. Compounds in which uranium is not associated with oxygen in the radical UO_2 (uranyl), as is well known, in general are non-luminescent. The best known exception to the above statement is canary glass, in which the uranium is probably present as a silicate in dilute solid solution in the glass. There are, to be sure, occasional references to uranium as a possible activator in the preparation of fluorescent combinations. Gans and Vanino,[1] for example, mention nitrates of uranium as increasing the brightness of luminous paints made of strontium or barium sulphates, but as inactive when calcium sulphate is used. Preliminary experiments made in the course of our studies[2] of the fluorescence of the uranyl salts (1919) indicated, moreover, that uranium may become an activator when dissolved in sodium phosphate. Those observations were the starting-point of the more systematic investigation to be described in this section, which is reprinted substantially unchanged from a recent report.[3]

SODIUM PHOSPHATE AS A SOLVENT

When microcosmic salt ($H,Na,NH_4.PO_4,4H_2O$) is fused, either in a crucible or on the platinum wire, the resulting glasslike bead shows no appreciable luminescence under photo-excitation or in the cathode tube. The addition of a uranium compound, even in quantities too small to give the bead body color, results, however, in a bright-green luminescence. Excessive heating destroys the power to respond to photo- or cathodo-excitation, and that this is due to the expulsion of water of constitution is evident, since on dissolving in water and heating again to complete dryness the luminescent power is restored. Merely allowing the hygroscopic salt to absorb the moisture from the air is not sufficient. The salt containing water must be subjected to suitable heat treatment before it will again fluoresce.

[1] Gans and Vanino. Journal für praktische Chemie, 1905.
[2] Nichols and Howes. Carnegie Inst. Wash. Pub. No. 298, 1919.
[3] Nichols and Slattery. Jour. Opt. Soc. Am., XII, p. 449, 1926.

The relation of brightness to concentration of a series of these preparations, as measured by means of an optical pyrometer of the heated-filament type, is shown in figure 54, in which abscissæ, plotted to a logarithmic scale, are molecules of uranyl phosphate, and ordinates are relative intensity of luminescence when the bead was excited by the radiation of a mercury arc filtered through a layer of

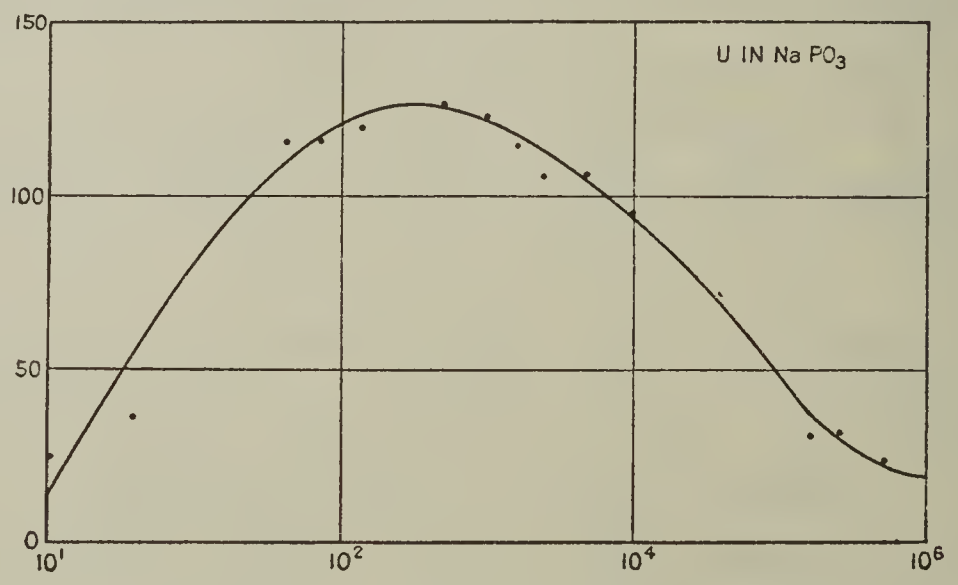


FIG. 54—Uranyl phosphate in sodium phosphate, showing the optimum

deep-purple glass (Corning). The *Bruninghaus optimum* is well defined at about 0.005 mole-fraction. At a concentration of 0.0001 the brightness was still nearly one-eighth of that of the maximum concentration.

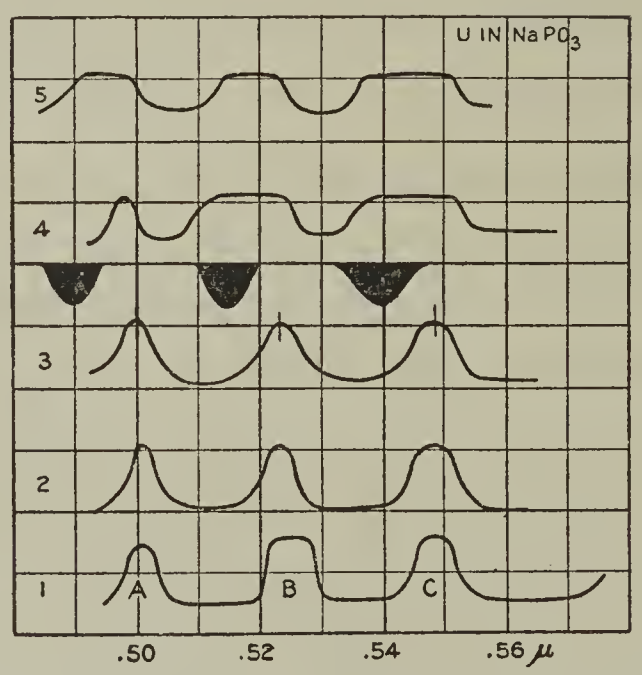


FIG. 55—Uranyl phosphate in sodium phosphate, crests and absorption bands

The *fluorescence spectrum* of this solid solution of uranium, probably in the form of the phosphate, shows three broad bands (*A*, *B*, *C*, fig. 55), easily discerned, with suggestions of a fourth and very feeble band in the yellow. Figure 55 will serve to indicate the approximate location and width of these bands, compared with the intervening dark regions, as they appear after five different kinds of heat treatment.

(1) The mixture, which was of the proportions to yield the optimum brightness, was heated in a platinum loop in the Bunsen flame until fusion occurred with formation of a bead. It was then immediately withdrawn from the flame and when cold was excited to fluorescence by the mercury arc through the screen of deep-purple glass. Under these conditions, bands *A*, *B*, and *C*, as determined by locating their edges, were narrower than the intervening spaces, and so far as could be seen had rather broad single crests. The suggestion of a fourth curve, only one edge of which could be located, and that roughly, is indicated.

(2) and (3) Two subsequent brief heatings similar to that described above and like (1), not sufficient to produce a bead which was transparent when cooled, brought about no apparent changes in the spectrum, excepting a more definite crest to bands *A* and *B* (see curves 2 and 3, in fig. 55).

(4) Upon further heating of the bead, just sufficient to clear it up and to render it transparent when cold, bands *B* and *C* were greatly broadened toward the shorter wave-lengths, the edges on the side toward the red remaining unshifted. Band *A*, however, was still quite narrow.

(5) The bead was returned to the flame and heated until it boiled no more. The result was to extend band *A* toward the blue until it was approximately as wide as *B* and *C*, which were not further modified. As has already been noted, prolonged heating beyond this stage renders the bead non-luminescent.

The diagram in figure 55 is intended to convey in a conventional way simply the location of the bands, the places of which correspond with those determined for a somewhat similar preparation in 1918,[1] their width, and the width of the intervening spaces; also, the fact that they appear in the spectroscope to be about equally bright. To determine the more intimate structure, detailed spectrophotometric measurements were made upon a bead the previous heat treatment of which corresponded approximately to stage (5) in figure 55.

The result which is given in figure 56 reveals something of this structure. It was found, as was to be expected from our knowledge of the luminescence spectra of the uranyl salts, that what appear to the eye to be simple bands (*A*, *B*, and *C*, fig. 55) are made up of several narrow components. These are only partly revealed, but since at the temperature of liquid air no further degree of resolution occurred, as had long since been found to be the case in the luminescence spectra of sodium phosphate,[2] a partial analysis was attempted on the basis of the spectrophotometric curve (fig. 56).

[1] Nichols and Howes. Carnegie Inst. Wash. Pub. No. 298, p. 142, 1919.
[2] *Ibid.*

Starting with the two best defined crests as a basis, those at 0.5045μ and 0.5188μ (see table XXXVII), we note that these have a frequency-interval of 54. While there are no other crests revealed which are equally spaced with these, we find that, assuming the existence of a set of crests thus spaced, the next members come at 0.4912μ on one side and at 0.5336μ on the other and that these coincide with the very square shoulders toward the violet of the broad bands *A* and *C*. Such a hypothetical set is indicated by the four short vertical lines labeled "Set 1" in figure 56.

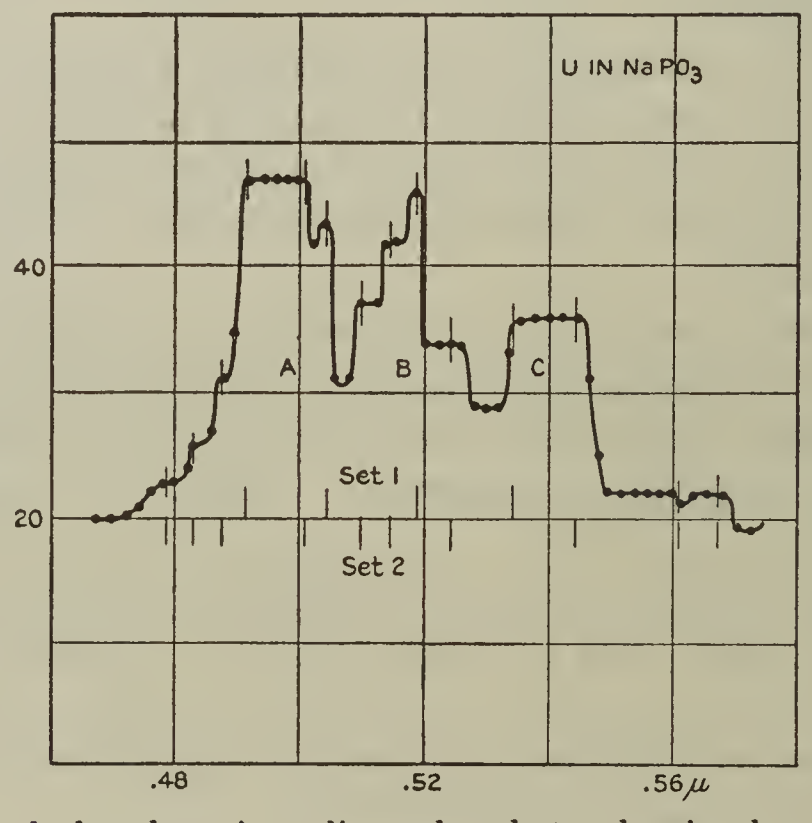


FIG. 56—Uranyl phosphate in sodium phosphate, showing location of crests

If two crests, also clearly present between the two above mentioned at 0.5096μ and 0.5145μ, which are not in step with set 1, but which have a frequency difference of 18 (or 54/3), are made a starting-point of another set, we find 10 members which correspond with the other square shoulders of the broad unresolved bands or with minor inequalities in the curve suggestive of submerged components. These are indicated by another set of short vertical lines labeled "Set 2." Both sets are given in table XXXVII. The frequency intervals are of course all 18, or some exact multiple of that number.

The consideration of the structure of this spectrum of uranyl phosphate in sodium phosphate, necessarily incomplete because of the overlapping of the components, suffices to show the dissimilarity between the luminescence of this solid solution and that of the uranyl salts. While the broad bands, considered as single, are separated by an interval characteristic of the uranyl salts (*i. e.*, 88) and are made up of narrower submerged components, there is no obvious repetition of the arrangement of these within the successive bands such as to give the striking and extraordinary homologous sets found in the spectra of the uranyl salts. Whether, if the spectrum could be resolved

by cooling, such an arrangement would appear, can not be determined from this preparation.

TABLE XXXVII—*Components of the luminescence spectrum of uranyl phosphate in sodium phosphate at +20° C.*

Set 1			Set 2		
μ	$1/\mu\times10^3$	Δ	μ	$1/\mu\times10^3$	Δ
			0.4790	2,088	
					18
			.4830	2,070	
					18
			.4873	2,052	
0.4912	2,036				54=18×3
		54=18×3	.5005	1,998	
.5045	1,982				36=18×2
			.5096	1,962	
		54=18×3			18
			.5145	1,944	
.5188	1,928				36=18×2
		54=18×3	.5241	1,908	
.5336	1,874				72=18×4
			.5445	1,836	
					54=18×3
			.5611	1,782	
					18
			.5669	1,764	

SODIUM BORATE AS A SOLVENT

A borax bead without admixture is nearly neutral. According to photographs made by Mr. P. A. Northrop in the course of his investigation, a cathodo-luminescence in the blue and extending into the ultra-violet is to be detected only after prolonged exposure. The spectrum is continuous. When impregnated with traces of a uranium salt, however, borax has a well-marked green fluorescence under photo-excitation.

The spectrum, as with sodium phosphate, is profoundly affected by the previous heat treatment. After a brief preliminary heating leaving the substance white and not fused, three bands are present. These are slightly broader than in the phosphate under similar conditions (fig. 55, *1*). They are almost identical with these as to position, however. (See curve *1* in fig. 57.) We may assign to the crests the locations marked by the short vertical lines.

TABLE XXXVIII

μ	$1/\mu\times10^3$	Δ
0.502	1,992	
		88
.526	1,904	
		88
.5505	1,816	

The determination is necessarily rough, but will suffice to indicate constancy of frequency difference and approximately the same interval as in figure 55. After heating the bead to fusion, but leaving it clouded, the bands are blended in one (fig. 57, *2*). Clearing the bead by further heating broadens the band in both directions (fig. 57, *3*).

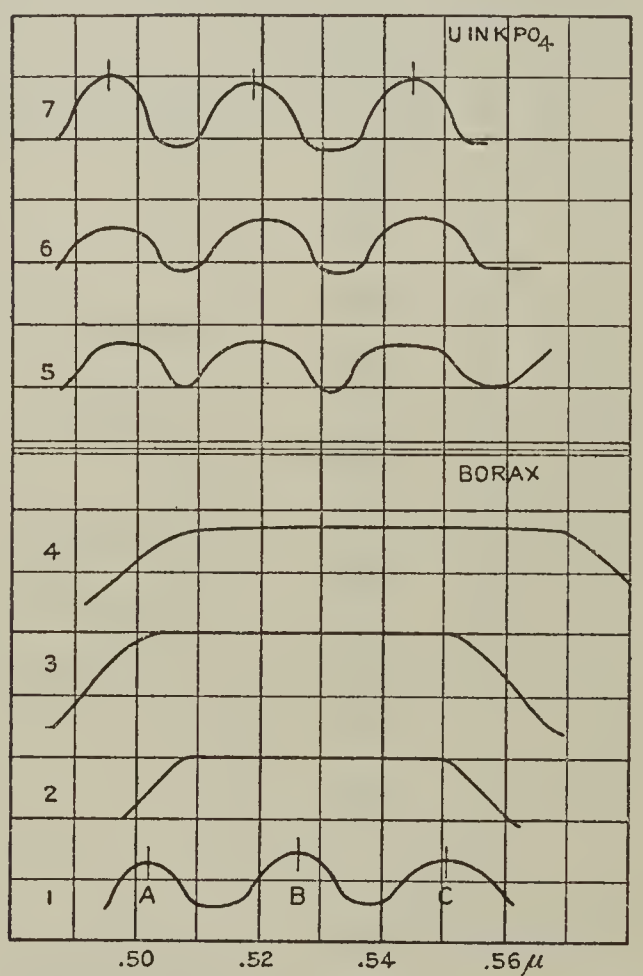


FIG. 57—Uranium in potassium phosphate and borax

When excited to luminescence at the temperature of liquid air, the band is shifted towards the red *by* at least *100* Å., and further broadened. As with the solid solution in sodium phosphate, continued heating causes complete loss of fluorescence, which is restored by the addition of water and suitable reheating.

POTASSIUM PHOSPHATE AS A SOLVENT

When potassium phosphate was substituted for sodium phosphate as the solvent of uranyl phosphate, the resulting bead was found to have a decidedly bluish-green luminescence, a change due to a shift of the bands *A*, *B*, and *C* toward shorter wave-lengths by about 65 Å. (See curves *5*, *6*, and *7* in fig. 57).

After the first stage of heating the bead was clear, after the second it was clouded, and after the third was clear again, changes which probably corresponded to successive losses of water as the material went through the transformations $KH_2PO_4.H_2O \longrightarrow KH_2PO_4 \longrightarrow KPO_3$. As will be seen from the curves, no conspicuous modifications in the spectrum occurred, excepting a slight shift of the bands towards the blue and an increase in the relative brightness of band *B* in the final stage. Further and more prolonged heating destroyed the luminescence, which, as in the case of the previous preparations studied, could be restored by the addition of water and reheating.

The distance between crests (assigning to them the places indicated by the vertical lines) was 91, but the difference, as compared with the difference of 88 for sodium phosphate and borax, while probably real, is in some doubt because of the great width of the bands.

SODIUM FLUORIDE AS A SOLVENT

The brightest and most striking of the luminescent substances included in the present investigation are those in which sodium

fluoride is used as a solvent. In color, at room temperature, they are a *vivid yellow,* instead of the green characteristic of the uranyl salts and of the other solid solutions in which uranium is the activator.

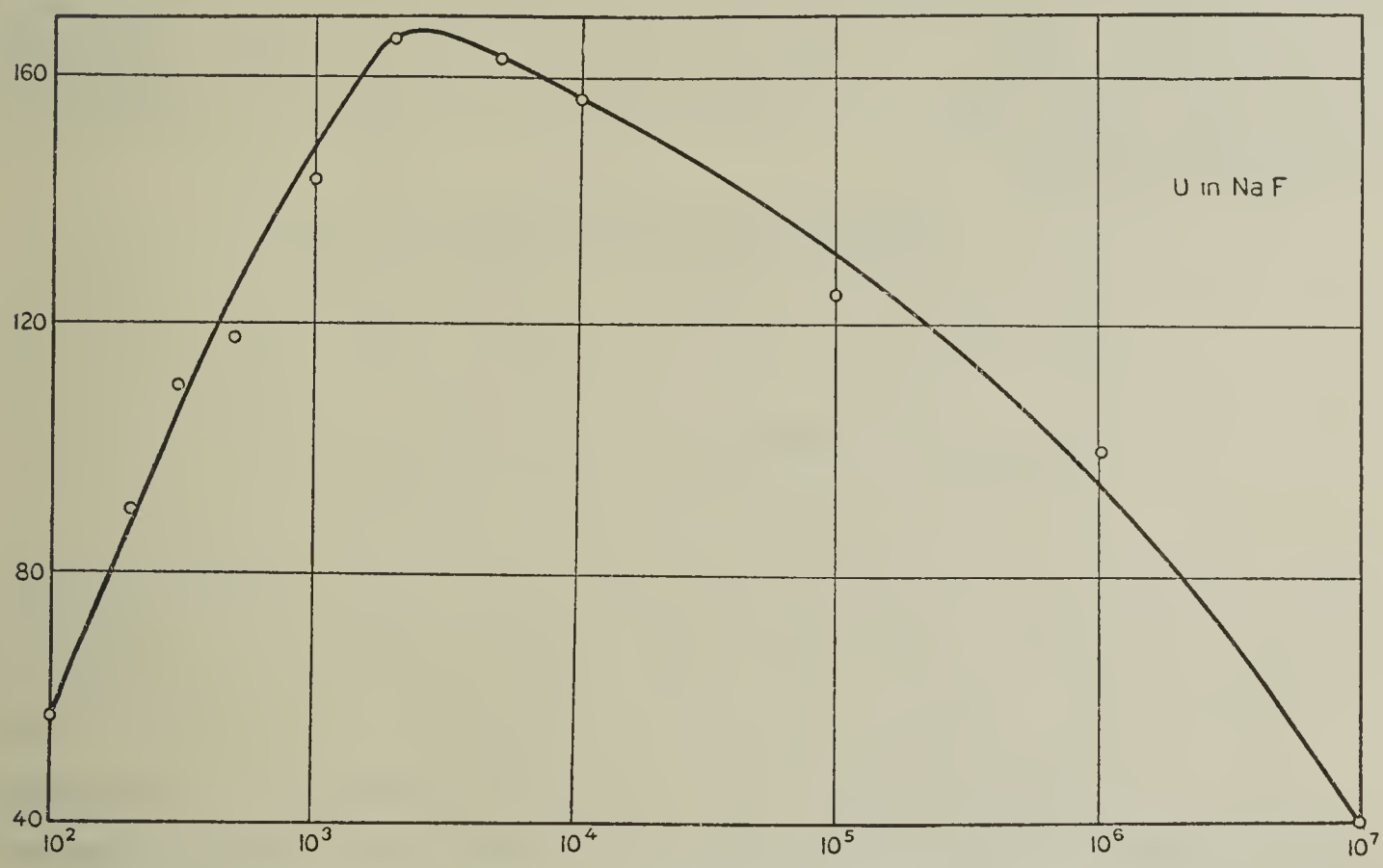


FIG. 58—Uranium in sodium fluoride, showing curve for the optimum

So effective is uranium in sodium fluoride that with 1 molecule in 10,000,000 the luminescence is still easily measured. The optimum brightness occurs at a dilution of 1 molecule to 2,000, as shown in figure 58, in which, as in the previous optimum curve (fig. 54), in order to represent the great range covered by the measurements, the curve is plotted to a logarithmic scale for the abscissæ, and where abscissæ are molecules of the solvent to one molecule of the activator (UO_2F_2).

THE SPECTRUM

Owing probably to the absence of water, these preparations are not appreciably sensitive to differences of heat treatment. We have to do therefore essentially with only one spectrum for a given temperature of observation, and do not have to consider the various stages described in previous paragraphs.

At room temperature the appearance of the spectrum does not suggest any close relation to the well-known spectra of the uranyl salts, in which each band is made up of the same components, the arrangement repeating itself over and over as we pass from red to violet. In the present case five rather broad bands are readily distinguished, with their group crests approximately as below. These are called *group crests* to distinguish them from the crests of their hidden components subsequently described.

These bands are not of equal breadth, nor are they equally spaced. There is a tendency to resolution, but this does not manifest itself in the same manner in the different bands. The two inner and brightest bands, in yellow-green and orange, are of by far the greatest intensity. Band *D* (0.557μ) shows a single crest somewhat toward the violet from the center, while its neighbor *C* (0.577μ) is obviously a doublet.

TABLE XXXIX—*Group crests*

Band	μ	$1/\mu \times 10^3$	Δ
A	0.634	1,577	
			73
B	.606	1,650	
			81
C	.577	1,731	
			64
D	.557	1,795	
			71
E	.534	1,872	

Instead of depicting these differences as has been done in figures 55, 56, and 57, we may proceed at once to the results of the spectrophotometric measurements indicated in figure 59. Here two curves

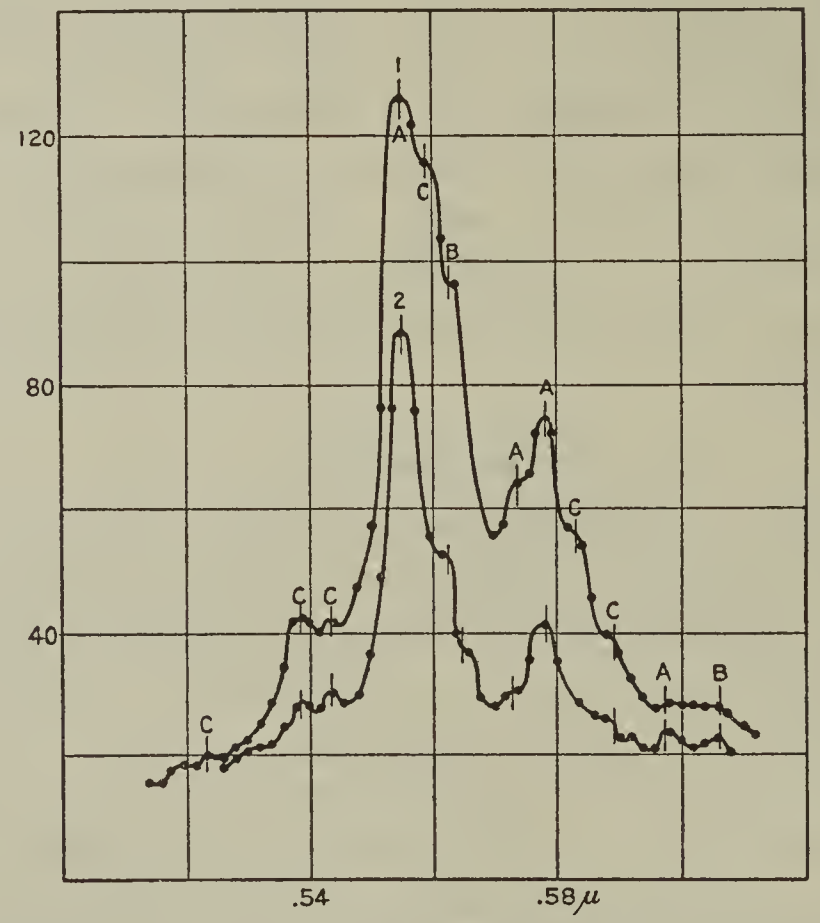


FIG. 59—Uranium in sodium fluoride, showing location of crests

are given: (1) for a dilution of 1 : 2,000; (2) for a dilution of 1 : 100,000. It will be seen that these curves are similar, excepting in such minor differences as may be ascribed to unavoidable variations in the intensity and quality of the excitation from the mercury

arc (through purple glass). The ratio of brightness of the two is also obviously of the order indicated in the optimum curve (fig. 58) for these two dilutions, *i. e.*, about 3 : 2.

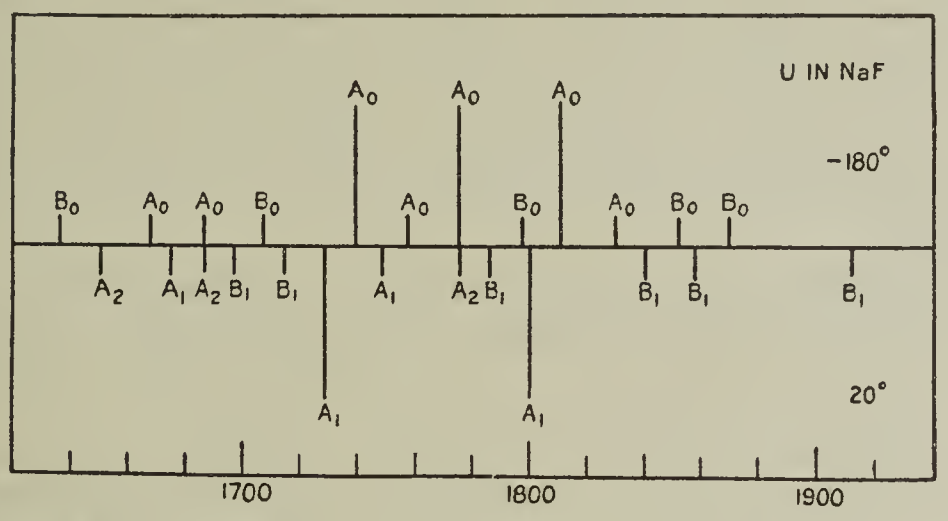


FIG. 60—Uranium in sodium fluoride at 20° and −180° C.

As to structure, we may readily pick out from the curves a number of more or less submerged components, and these (like those of the spectrum of the solution in sodium phosphate) can be ranged in sets with frequency differences which are multiples of the same or very nearly the same interval, *i. e.*, 18. (See table XL.)

TABLE XL—*Components of the luminescence spectrum of uranyl fluoride in sodium fluoride, at 20° C.*

Set A_1			Set A_2			Set B_1		
μ	$1/\mu\times10^3$	Δ	μ	$1/\mu\times10^3$	Δ	μ	$1/\mu\times10^3$	Δ
			0.6064	1,649				
0.5974	1,674				36			
		54	.5935	1,685				
[1].5785	1,728					0.5896	1,696	
		18			90			18
.5727	1,746					.5834	1,714	
		54	.5634	1,775				72
.5555[1]	1,800					.5599	1,786	
								54
						.5435	1,840	
								18
						.5382	1,858	
								54
						.5230	1,912	

[1] The principal crests as shown in figure 59.

The method of locating the short vertical lines in figure 59, which are intended to show such crests wherever the observations afford a suspicion of their whereabouts, was as follows: It having been noted that the two chief peaks on both curves, *i. e.*, at 0.5555μ and 0.5785μ have a frequency difference of 72, which is a multiple of the interval 18, that had been found characteristic of the spectrum of uranyl phosphate in sodium phosphate, other members of a set having as fre-

quency-intervals multiples of 18 were sought for by inspection of the curves. These were marked by vertical lines (A) and recorded in table XL as set A. Similarly a set (B) was formed from the minor crest at 0.6064μ, which crest is clearly indicated in curve 2, and a third set (C) was based upon the two crests at 0.5896μ and 0.5834μ, which are 18 frequency units apart. These three sets cover all the submerged crests which can be located with any degree of probability from the curves.

At the temperature of liquid air the luminescence spectrum of uranium in sodium fluoride, unlike those previously described in this paper, is resolved into narrow-line-like components. The salient feature of this resolved spectrum is a group of three strong, equidistant bands with an underlying structure of relatively feeble intensity, some components of which are so weak as to be difficult objects in the field of the spectroscope.

This strong trio is indicated in figure 60 by the *tall* vertical lines A_0, A_0, A_0. The outer members are the same distance apart as the principal crests in the spectrum at 20°, the location of which is shown in figure 60 by the tall verticals *below the line*, A_1, A_1. From these they are, however, displaced nearly 11 frequency units toward the violet. Since the frequency difference is 72, these strong bands with the intermediate companion midway between them may be regarded as members of a set with the interval 18 and in fact four of the other bands of this spectrum (see table XLI) and the short vertical lines marked A_0 in figure 60 are found to belong to such a set. The remaining five bands upon which readings could be made form another set, B_0, of like frequency interval.

The vertical lines below the horizontal line in figure 60 are plotted from table XL. Of these, the sets A_1 and B_0 have throughout the same displacement from the corresponding members of A_0 and B_0 as the principal peaks at 20° from the strong lines at —180°, *i. e.* (as pointed out above), about 11 frequency units, while two members of the three in set A_2 coincide, within the errors of observation, with A_0.

This coincidence indicates that the displacement on cooling *is not a shift* of the bands, in the ordinary sense, but is due to a subsidence of certain bands as we pass from room temperature to that of liquid air, and the enhancement of others. This is a phenomenon which has long since been found to be characteristic of the spectra of the uranyl salts.[1]

In the foregoing description of the method employed in the study of the fluorescence spectrum at room temperature, as has already been explained, the existence of a frequency-interval of approximately 18

[1] Nichols and Howes, l. c. p. 68.

was assumed, and it was sought to determine how well such an interval fitted the crests and submerged components of the spectrophotometric curve. In the case of the spectrum at —180°, however, where direct settings of the bands could be made to within about one frequency unit, the opposite and more usual method of direct readings was employed, the results of which are given in table XLI. That the two methods are about equally good appears from the uniformity of the displacements of A_1 from A_0 and of B_1 from B_0 throughout the spectrum. That the interval for —180° is very close indeed to that assumed for 20°, may be shown by taking the distance between the end members of sets A_0 and B_0.

For A_0 we have: 1,829.5—1,667.6=161.9 and 161.9/9 =17.99
For B_0 we have: 1,869.2—1,635.0=234.2 and 234.2/13=18.02

In table XLI it will be seen that individual departures of the frequency-interval from 18 or some exact multiple thereof are never as great as one frequency unit, that for set B_0, they never exceed 0.2, and that the wide departures in the two last intervals are to be ascribed to a slight mislocation (by 2 Ångström units) of the band 0.5523μ, which is believed to be due to a slight irregularity in the scale of the direct-reading drum of the spectrometer not adequately corrected for in the calibration.

TABLE XLI—*Components of the luminescence spectrum of uranyl fluoride in sodium fluoride at −189°*

Set A_0			Set B_0		
μ	$1/\mu\times10^3$	Δ	μ	$1/\mu\times10^3$	Δ
			0.6116	1,635.0	
0.5996	1,667.6				
		18.2			71.8=18×4−0.2
.5932	1,685.8				
		53.3=18×3+0.3	.5859	1,706.8	
.5750[1]	1,739.1				
		17.8			
.5692	1,756.9				90.2=18×5+0.2
		18.3			
.5632[1]	1,775.2				
		35.4=18×2−0.6	.5565	1,797.0	
.5523[1]	1,810.6				
		18.9			54.2=18×3+0.2
.5466	1,829.5				
			.5402	1,851.2	
					18.0
			.5350	1,869.2	

[1] Strong.

The interval 18, which seems to be applicable to the various spectra considered in this paper, is of the same order as the intervals found to exist between neighboring components in the fluorescence of

the uranyl salts. It is also incidentally almost exactly the Tanaka interval[1] for uranium, as found by that investigator in his determination of the relation between the frequency interval in cathodo-luminescence and the atomic weights of the activating element. (See Chapter III.)

CALCIUM FLUORIDE AS A SOLVENT

The fact that fluorspar is luminescent and often contains as activators traces of the rare-earth elements such as samarium,[2] led us to try calcium fluoride as a solvent for uranium. To this end a number of procedures were used.

(*a*) Powdered fluorite was heated upon a platinum wire to fusion, the bead thus formed was dipped into a dilute solution of uranyl chloride, and again brought to the molten state. When exposed after cooling to excitation by the iron spark, by a mercury arc in quartz, or by cathode bombardment, it showed a fine green luminescence.

(*b*) One corner of a crystal of fluorspar, nearly colorless, was moistened with the uranyl-chloride solution and brought to incipient fusion in an oxyhydrogen flame supplied with a minimum of oxygen. Under photo-excitation the fused portion glowed with the characteristic green luminescence.

(*c*) Powdered UO_2F_2 was mixed with CaF_2, also powdered, in the desired proportions, and the mixture was heated in the oxyhydrogen flame.

(*d*) In an attempt to avoid the great variations in brightness exhibited by beads prepared in the foregoing ways, UO_2NH_4F was dissolved in water and the calcium fluoride was moistened with this solution before heating. No greater uniformity of product, however, was obtained by this process, and it was soon found that the difficulty lay in the conversion of portions of the fluoride into calcium oxide. Uranium, as opposed to other activators used with calcium fluoride, became inert when the solvent is converted into the oxide. This unexpected result was verified by oxidizing fluorescent preparations and thus rendering them inert and by treating inert solid solutions of uranyl fluoride in CaO with hydrofluoric acid, thus changing the oxide into the fluoride, and then applying heat treatment, whereupon they became fluorescent.

The optimum value—The difficulty just mentioned in controlling the brightness of beads of a given concentration complicates the determination of the optimum, but by giving particular attention

[1] T. Tanaka. J. O. S. A., VIII, p. 287, 1924.

[2] See the extended investigations of Crookes, LeCoq de Boisbaudran, Urbain, and others, and the recent studies by Miss Frances G. Wick (Phys. Rev. (2), XXIV, 272–282, 1924).

to uniformity of heat treatment the results plotted in figure 61 were obtained. As in previous curves for the optimum, abscissæ are on a logarithmic scale, while ordinates are plotted on a direct scale. The maximum brightness is seen to occur with 1 molecule of uranyl fluoride to 900 of the solvent, a value between that for sodium phosphate and that for sodium fluoride.

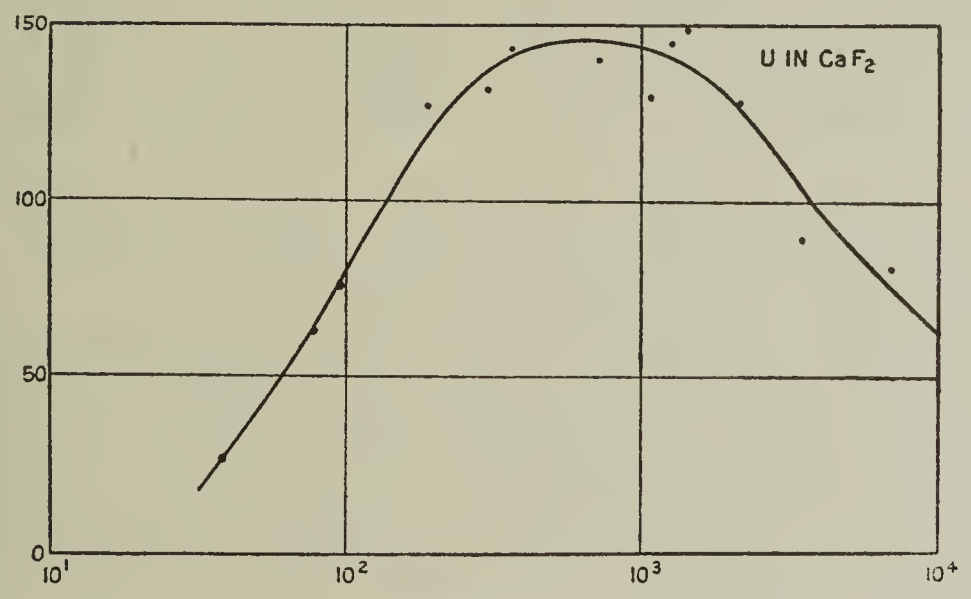


FIG. 61—Uranium in calcium fluoride, curve for the optimum

The spectrum of uranyl fluoride in calcium fluoride presents to the eye the appearance of a single broad band rather than of a group of bands. It would not be possible to map it definitely, as the previous spectra were mapped, by assigning boundaries to its group-

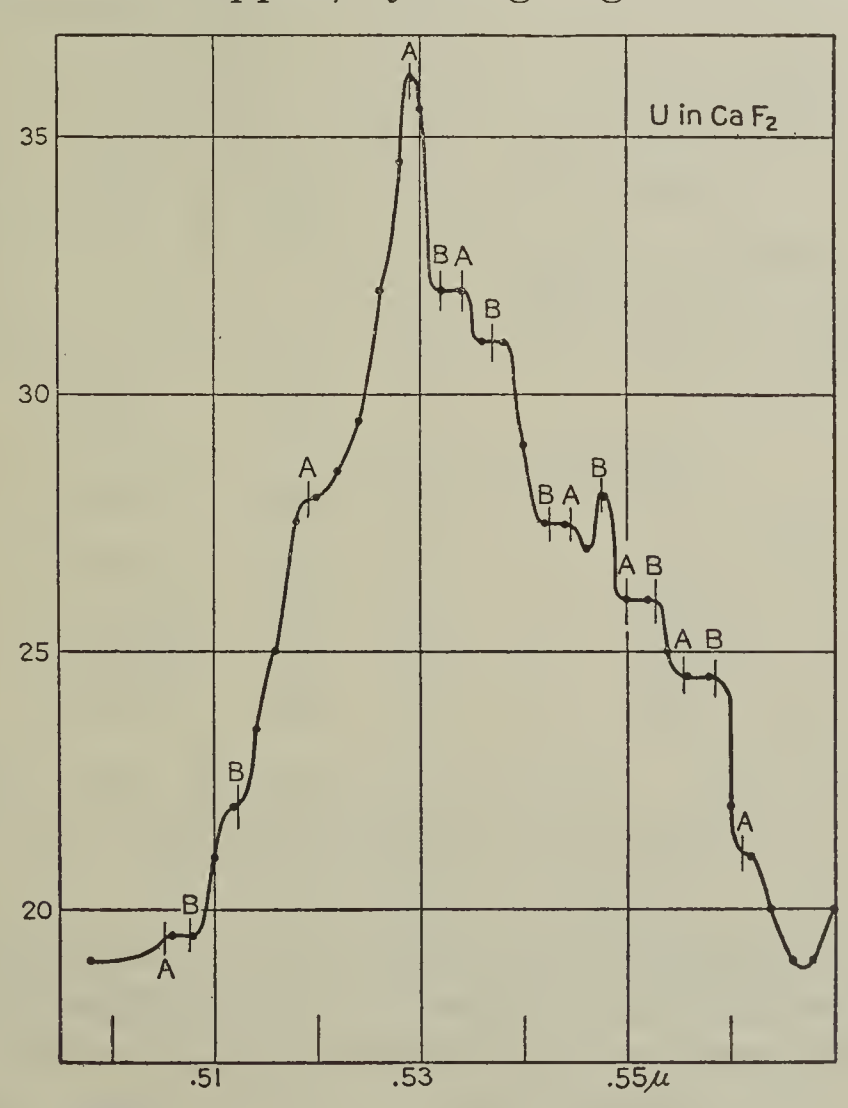


FIG. 62—Uranium in calcium fluoride, showing location of crests

components. Still there are suggestions of structure and a spectrophotometric determination shows a well-developed crest (fig. 62) and numerous semi-submerged components.

If we apply the same method as in the case of the spectrum of uranyl fluoride in sodium fluoride, basing one set upon the principal crest at 0.5291μ and another upon the minor crest at 0.5476μ it is found that the frequency interval 18 fits the curve as well as in the previous cases. (See also table XLII.) If we assume that the minor irregularities in the curve at 0.5065μ, 0.5330μ, 0.5432μ, 0.5515μ, and 0.5570μ represent single components, four sets will be required, but if they are taken to be doublets sets A and B suffice. The latter assumption is used in the figure and table.

After the curve in figure 62 had been plotted from the spectrophotometric readings and set A in table XLII had been compiled, it was noted that *set A is identical with set A_1 in table XL,* the position assigned, by inspection of the curve, to the principal crest being 90 units towards the violet from the principal crest of the curve for U in NaF (fig. 58).

TABLE XLII—*Luminescence spectrum of uranyl fluoride in calcium fluoride at 20° C.*

Set A			Set B		
μ	$1/\mu\times10^3$	Δ	μ	$1/\mu\times10^3$	Δ
0.5051	1,980				
		54=18×3	0.5076	1,970	18
.5192	1,926		.5123	1,952	
		36=18×2			72=18×4
.5291[1]	1,890		.5319	1,880	
		18			18
.5342	1,872		.5370	1,862	
		36=18×2			18
			.5423	1,844	
.5447	1,836				18
		18	.5476[1]	1,826	
.5500	1,818				18
		18	.5531	1,808	
.5555[2]	1,800				18
		18	.5586	1,790	
.5612	1,782				36=18×2
			.5701	1,754	

[1] Crest. [2] Crest of U in NaF.

The positions assigned the components in set B, table XLII, do not coincide absolutely with those of the corresponding set in table XL, but the discrepancy is of the same order as the uncertainty in locating the various components. In other words, were the curves

for both spectra replotted from the spectrophotometric data and the components designated by inspection without cognizance of the values previously assigned to them, it is quite likely that either of the new sets thus determined would depart from the original settings by an amount as great as the discrepancy between sets as given in the tables. There is, in short, reason to believe that these sets are likewise identical and that the two spectra *are made up of the same components and differ only in the relative brightness of their bands.*

The same remark applies to the spectrum of uranyl phosphate in $NaPO_3$ (fig. 56), where, however, it is set 2, instead of set 1, which coincides with the A sets of the other two solutions. It is to be inferred from this that the main crest lies at the right edge of the group-band A at 0.5008μ. The departures of set 1 (fig. 56 and table XL) from the A sets (which happen to be in complete identity) is of the order of *one* frequency unit, which is well within the errors of plotting. The distance between sets for the three spectra is likewise the same, within experimental errors, *i. e.,*

Set 1 to set 2	Table XL	11 units
Set A to set C	Table XLI	11 units
Set A to set B	Table XLII	12 units

In a word, we have in the foregoing data an excellent illustration of the *principle of essential identity.*

SOME MISCELLANEOUS OBSERVATIONS

(1) *Molecular weights of the solvents and wave-length of main crests*—The color of luminescence of U in NaF is yellow, in CaF_2, $NaPO_3$, and borax, green, and in KPO_3, blue-green, which suggests a shift of color with the molecular weight. Taking the three solutions for which the position of the main crest has been determined,

Solvent	Molecular weight	Crest (μ)
NaF	42	0.5555
CaF_2	78.07	.5291
$NaPO_3$	102.4	.5008

we have nearly an inverse linear relation. (See figure 63.) In KPO_3, with a molecular weight of 118.5, the crest of the spectrum should lie at about 0.49μ (see the hypothetical position marked *X* upon the extrapolated curve). This would place the crest in band *A* of figure 57 to the right hand of the center as there indicated, which is the probable location. Bruninghaus,[1] and later, Tanaka,[2] noted

[1] L. Bruninghaus. Comptes rendus, 144, 1040–1042, 1907; at greater length in Le Radium, 4, 416–429, 1907.

[2] T. Tanaka. J. O. S. A., VIII, p. 294, 1924. See also figures 24 and 25, Chapter III.

a similar relation between the maximum of brightness in the luminescence of solid solutions of copper in various salts of calcium.

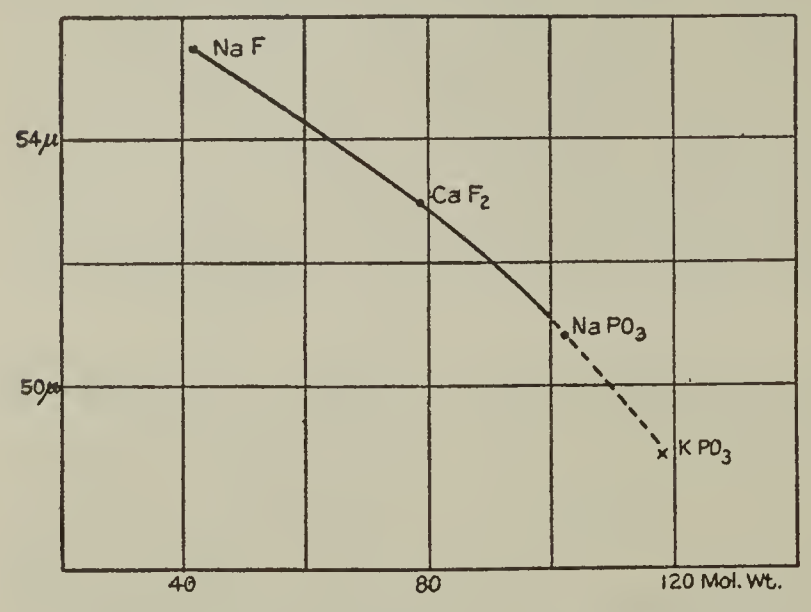


FIG. 63—Wave-length of maximum brightness against molecular weight of solvent

(2) *Phosphorescence and Thermo-luminescence*—None of the substances considered in this paper show a noticeable after-glow at 20° or at —180° as observed without the aid of a phosphoroscope, and none of them are perceptibly thermo-luminescent. Upon exposure to X-rays, *to which they are inert so far as any direct effect is concerned,* it was found that the solutions in NaF and CaF_2 after exposure showed decided thermo-luminescence, in which respect they resemble fluorites and calcites previously studied.[1] Solutions in NaF, after exposure to X-rays for one hour, showed a *bluish green* thermo-luminescence, even in the case of a bead having a proportion of 1 : 10^7, when heated to an approach to a dull red. Solutions in CaF_2 gave a bright-green thermo-luminescence (after X-ray treatment) in which the banded structure of the spectrum was momentarily visible. This brief glow was followed by a glow of slow decay, yellow or orange in color and doubtless due to traces of other activators present in the solvent, as it was also obtained with beads containing no uranium. Solutions in $NaPO_3$, when exposed to X-rays, acquired a *pink* body-color. Their photo-luminescent properties were not perceptibly modified, and they showed *no thermo-luminescence.*

Samples made by impregnating $CaSO_4$ with traces of a uranyl salt in solution and igniting at moderate heat were inert to photo-excitation, but after exposure to X-rays for one hour there was bright-green thermo-luminescence of rapid decay. This experiment was tried because it was known that thermo-luminescence could be produced when manganese was used as an activator.

(3) *Previous exposure to ultra-violet radiation* was applied to the various solutions, as a possible substitute for X-rays, but no thermo-luminescence was thus produced.

(4) *Possible effect of dissolved platinum*—Since in the case of these solvents, particularly of the sodium phosphates, platinum is more or less attacked, the question of the influence of dissolved platinum upon

[1] Frances G. Wick. Phys. Rev., XXV, p. 588, 1925. [See also Chapter VII, Section IV.]

the luminescence arose and tests were made in which platinum compounds were introduced into the solutions. The results were entirely negative.

SUMMARY

(1) Traces of a compound of uranium when brought by fusion into solid solution in $NaPO_3$, KPO_3, borax, NaF, or CaF_2 render the substance luminescent under photo- or cathodo-excitation.

(2) There is a definite optimum proportion for each solvent which gives the maximum brightness.

(3) The spectra of these solid solutions consists of several bands, each of which is made up of numerous overlapping and semisubmerged components, but the spectral structure is distinctly different from that of the uranyl salts.

(4) The components may be arranged in two or more sets, the frequency interval between members of a given set being constant or some exact multiple of a constant.

(5) The frequency interval (18) is the same for all sets of each spectrum and for the different spectra.

(6) The sets in the spectra of preparations in which $NaPO_3$, NaF, and CaF_2, respectively, are the solvents are identical in position, so that these spectra may be regarded as made up by the same components and as differing only in the *relative brightness* of the components.

(7) The position of the brightest component which determines what may be called the *main crest* of each spectrum is shifted toward the violet with increase of the molecular weight of the solvent, so that the color of luminescence goes over from yellow for NaF into green for CaF_2 and $NaPO_3$, and into blue-green for KPO_3.

(8) The phosphorescence of these preparations is of the vanishing type.

(9) They are inert under X-rays, but after exposure to X-rays they become thermo-luminescent.

(10) At the temperature of liquid air the spectra of solutions in NaF are resolved and those in CaF_2 partially resolved, while those in the other solvents remain unresolved.

II. RARE EARTHS AS ACTIVATORS

[Describing experiments of E. L. Nichols and H. L. Howes.]

The observations to be recorded in this section were made upon salts of samarium, europium, thulium, dysprosium, terbium, and of neodymium, praesodymium, yttrium, and erbium, prepared by Professor C. James. Traces of these elements (whatever be the combination in which they occur as the result of the various heat treatments applied) were put into solid solution in various solvents, *i. e.*,

[1] Nichols and Howes. Jour. Opt. Soc. Am., XIII, 573-587, 1926.

(1) CaF_2 or CaO; (2) borax glass (from borax), $NaPO_3$ (from microcosmic salts), NaF; (3) Al_2O_3.

The three solvents mentioned under (2) were used in the form of "beads" on platinum wire into which the activator could be introduced readily in the desired amounts. The attempts to activate such beads by means of the rare earths were suggested by the interesting results obtained in the study of *uranium as an activator*.[1]

Since most of the elements mentioned above have been studied in considerable detail by Crooke, Le Coq de Boisbaudran, Urbain, and others, there will be given here only such observations as are thought to be new or to afford confirmation or suggest modification of the conclusions of the earlier workers in this field.

The luminescence spectra were observed and roughly mapped by means of a hand spectroscope with direct-reading wave-length scale. All finer details, for the study of which this instrument was inadequate, were left for subsequent study. It may be remarked, however, in this connection that except for the accurate location of very narrow line-like bands and the resolution of close groups, an optically good instrument of small dispersion has many advantages, especially in a rapid preliminary survey of new spectra. Excitation to luminescence was by the iron spark and by cathodo-bombardment, respectively.

LUMINESCENCE OF THE VARIOUS COMBINATIONS

In table XLIII is recorded for comparison the effects produced by impregnating with traces of various rare earths the solid solvents already enumerated.

TABLE XLIII—*Effect of the rare earth elements as activators*

Activator	Solvent	Luminescence			
		Photo		Cathodo	
		Color	Remarks	Color	Remarks
Thulium.....	$NaPO_3$	.....	.....	.....	.....
	NaF	.....	.....	Red.....	Broad bands
	Borax	Pale apple-green	Narrow bands...	Violet.....	Narrow bands
	CaF_2	.....	.....	Bright.....	Numerous line-like bands (table XLIV)
	CaO	.....	.....	Fine blue.....	Many line-like bands
	Al_2O_3	.....	.....	Blue(1).....	v.d. Continuous sp.

(1) After heating to 900° a dim white.

[1] Nichols and Slattery. Jour. Opt. Soc. Am., XII, p. 449, 1926; also section I of this chapter.

TABLE XLIII—*Effect of rare earth elements as activators*—Continued

Activator	Solvent	Luminescence			
		Photo		Cathodo	
		Color	Remarks	Color	Remarks
Europium.....	$NaPO_3$	Pink.....	.....	Red.....	Narrow bands (table XLV)
	NaF	.....	.....	Red.....	Continuous sp. 0.618, 0.625
	Borax	Cherry red..	Bright.....	Ruddy.....	
	CaF_2	Ruddy.....	Line-like bands..	Ruddy.....	Very complex (table XLVI)
	CaO	Ruddy.....	Bands very bright, line-like	Ruddy.....	Bands very bright, line-like
	Al_2O_3	.....	Line-like sp.v.d..	.....	Line-like (table XLVII)
Dysprosium...	$NaPO_3$	Opalescent..	.....	.....	.....
	NaF	.....	.....	Orange.....	Bright bands on continuous background, 0.556, 0.540 and 0.480
	Borax	Green.....	Line-like bands..	Green.....	Line-like bands
	CaF_2	.....	Very bright, line-like bands	.....	Very bright, line-like bands
	CaO	.....	Very bright, line-like bands		Very bright, line-like bands
Terbium.....	$NaPO_3$	.....	.....	.....	.....
	Borax	Green.....	Very bright.....	Green.....	Very bright
	CaF_2	.....	.....	Yellow-green..	Bright line-like bands
	CaO	.....	.....	Yellow-green..	Bright line-like bands
Samarium.....	$NaPO_3$	Red.....	Narrow bands at 0.647, 0.602, and 0.542	Red.....	Narrow bands at 0.647, 0.602, and 0.542
	NaF	.....	.....	Red.....	Very dim
	Borax	Red.....	Table XLIX....	Red.....	Table XLIX
	CaF_2	Red.....	.....	Very bright...	Do.
	CaO	Red.....	.....	Very bright...	Do.
Yttrium.....	$NaPO_3$	Green blue..	Dim.....	.....	.....
	NaF	.....	.....	White.....	Continuous sp.
	Borax	.....	.....	White.....	Very dim
	CaF_2	Purple.....	.....	Ruddy.....	Broad bands in red, green, and violet
	CaO	.....	.....	Blue.....	Terbium bands on continuous background
Neodymium...	$NaPO_3$	.....	.....	.....	.....
	NaF	Blue.....	.....	Red.....	Continuous sp.
	Borax	.....	.....	.....	.....
	CaF_2	.....	.....	.....	Shows samarium
	CaO	.....	Not recorded....	.....	Not recorded
Præsodymium.	Borax	.....	.....	.....	.....
	CaF_2	.....	.....	Orange-red....	Very bright spectrum highly resolved, with many line-like bands
Erbium.....	Borax	Green.....	Terbium lines...	.....	Very dim
	NaF	Green.....	Continuous sp...	.....	.....
	CaF_2	.....	.....	.....	Terbium lines, no continuous sp.

In the case of the first five elements listed in table XLIII, solutions in calcium oxide were found to be more brilliantly luminescent than solutions in the other solvents mentioned, although CaF_2, the activity of which may be due to superficial conversion of the surface into the oxide, was almost as good a solvent. The solutions in CaO were made by dissolving the rare-earth salt in nitric acid, diluting the solution, moistening powdered calcium carbonate with a sufficient quantity of the solution to give approximately the optimum proportions (say 0.2 per cent), and heating in a porcelain crucible to redness (about 700°). Thus prepared they were, in general, exceedingly brilliant in the cathode tube and gave spectra in which the bands were much more nearly line-like and better defined than those depicted by Urbain and the other earlier observers. These spectra are, indeed, only to be compared in beauty with those obtained by Miss F. G. Wick,[1] who heated to incipient fusion fluorspars containing samarium and other of the elements of that group. Whether the quality of the spectra thus obtained is to be ascribed to the unusual purity of the activating elements must for the present be regarded only as a surmise.

DOMINANCE AND SUPPRESSION

The tendency recorded by earlier writers for certain activators to suppress the luminescence due to other elements present in the solvent was strikingly confirmed by some of our observations. For example, the calcium oxide used in our preparations glows strongly under cathodo-excitation, with the characteristic red-yellow color due to the presence of manganese, as seen in the calcites from Franklin Furnace and from many other localities.[2] The spectrum of this glow, as is well known, is so broad-banded as to be practically continuous. When any one of the first five rare earths in table XLIII was added and the mixture was treated as above described, the continuous spectrum disappeared almost completely, leaving only the line-like bands produced by the activating action of the rare earth.

A striking instance of this selective activation was observed when neodymium was introduced into CaO. The spectrum invariably obtained was that of samarium. In the separation of præsodymium from neodymium, as is well known, samarium tends to go into the same fraction as the latter element. It is, therefore, the impurity chiefly to be expected in samples of neodymium. The neodymium used in this investigation was exceptionally pure, so that the solid solution of neodymium in calcium oxide probably contained only a few parts in a hundred thousand of samarium, a quantity sufficient,

[1] Frances G. Wick. Physical Review (2), XXIV, p. 272, 1924; also Chapter V, section III, of this treatise.

[2] Nichols, Howes and Wilber. Physical Review (2), XII, p. 351, 1908.

however, to suppress completely the luminescence due to all other possible activators which may have been present. It is probable that the amount of præsodymium present in such a preparation under the conditions described would exceed that of samarium, but the line-like and characteristic præsodymium spectrum was not to be seen. On the other hand, the samples of præsodymium doubtless contained traces of both neodymium and samarium, but the luminescence of both these activators was suppressed. It would appear, therefore, (1) that the luminescence of neodymium is suppressed by minute traces of either samarium or præsodymium; (2) that traces of samarium will suppress the luminescence due to traces of præsodymium when the dilution is of the same order, but that where præsodymium greatly preponderates the samarium bands are suppressed.

Yttrium and erbium afford other interesting illustrations of dominance and suppression. When yttrium is in solid solution in CaF_2 the line-like luminescence bands of terbium, which is present as a minute impurity, are suppressed, whereas in CaO the terbium bands dominate. On the contrary, the luminescence of erbium in CaF_2 is suppressed and the terbium spectrum comes out strongly. A comparison of the cathodo-luminescence of preparations of terbium and of dysprosium in CaO was also instructive in this connection. The dilution of these preparations was approximately equal, *i. e.*, 0.002 : 1, and they were prepared in a similar manner. The luminescence of dysprosium contains a prominent band in the red (0.675μ), whereas terbium has no bands of wave-lengths longer than the group at 0.625–0.627μ. The dysprosium spectrum, according to the measurements of Urbain,[1] terminates toward the shorter wave-lengths with the group at 0.565–0.595μ, while the spectrum of terbium extends throughout the blue and violet. In the case of the preparations used in this investigation, however, the dysprosium spectrum, in addition to the dysprosium bands, contained the terbium bands also, including those of shorter wave-lengths. The terbium spectrum, on the other hand, was devoid of dysprosium bands. This might be taken to indicate that the terbium was quite free from dysprosium, which was unlikely, or that a minute trace of terbium in the presence of a relatively much larger amount of dysprosium is capable of giving its characteristic spectrum, whereas in the presence of larger amounts of terbium dysprosium is inert. In a word, in a solution where terbium predominates the dysprosium bands disappear; in a solution in which dysprosium predominates both spectra appear. A description of the luminescence of terbium follows in the section on spectral structure.

[1] Urbain. Ann. de Chimie et de Physique, 8, 18, p. 222, 1909.

PERSISTENT PHOSPHORESCENCE AS A CRITERION

Under the conditions of these experiments the following very simple criterion for terbium in the presence of dysprosium was discovered: It was noticed that after the close of excitation the bands of the terbium spectrum persisted, whereas those due to dysprosium vanished at once. In the after-glow the spectrum of dysprosium is therefore absent, leaving that of terbium behind. In the intervening regions in the green and yellow of the spectrum, where the groups of bands due to these two activators overlap, this affords a convenient means of identification which is applicable to all the components which are strong enough to be seen in the phosphorescent after-glow.

SPECTRAL STRUCTURE

(1) Thulium

(*a*) *In NaF* with a sufficient admixture to give the bead a very faint yellow body-color, the spectrum under cathode bombardment showed two broad, overlapping bands, the location of which was approximately as follows: Edge, 0.555μ, crest, 0.575μ; min., 0.587μ; crest, 0.610μ; edge, 0.655μ. The frequency numbers ($1/\mu \times 10^3$) of the two crests are 1,739 (set A, table XLIV) and 1,629 (set C, table XLIV). After bombardment the bead was found to have acquired a pale pink body-color. It was observed that beads of NaF containing Tm were clouded when cold, became clear when fused in the hydrogen flame, and at a much higher temperature clouded up again and gave off an intense white light. The discussion of the visible emission accompanying this and other transformations occurring in these beads is reserved until later.

(*b*) *In* CaF_2—To a sample of the fluoride (from Kahlbaum) which when fused to a bead without admixture had, after cooling, a bright cathodo-luminescence with continuous spectrum, a trace of thulium oxide was introduced. The continuous spectrum was completely suppressed, as in the examples mentioned on a previous page, and a spectrum consisting of numerous line-like bands appeared. The detailed study of this spectrum is reserved until later. A preliminary survey with the hand spectroscope gave locations for the more conspicuous bands, as shown in table XLIV.

TABLE XLIV—*Bands in the spectrum of thulium in solid solution in CaF_2*

Set A			Sets B, C, and D			
	$1/\mu\times10^3$		Set		$1/\mu\times10^3$	
0.660	1,515	111=77×16−1				
.615	1,626	98= 6×16+2	B[1]	0.520	1,923	
.580	1,724	49= 3×16+1				
.564	1,773	64= 4×16+0	C	.455	2,198	64=4×16+0
.544	1,837	32= 2×16+0		.442	2,262	
.535	1,869	272=17×16+0				
.467	2,141		D[1]	.490	2,041	
Interval (from extremes)		16.05				

[1] To designate a single band as a member of a *set* of which no other members have been found may seem unwarranted, but our knowledge of such spectra would indicate the improbability of individual bands not thus connected. Band 1,923 (set B) has in fact been found to belong to a set of emission bands whose relation to the luminescence of thulium is to be considered elsewhere.

(*c*) *In CaO*—When prepared as already described, the spectrum under cathodo-bombardment consisted of many fine line-like bands. The ruddy fluorescence characteristic of the CaO and due to traces of manganese was totally suppressed. The spectrum, which was evidently not identical with that obtained when CaF_2 was the solvent, has not yet been mapped.

(*d*) *In Al_2O_3*—Using a procedure similar to that already described but with Al_2O_3 (from alum) instead of $CaCO_3$, a very feeble blue cathodo-luminescence was obtained having a spectrum in which the bands were barely discernible. On further heating to about 900°, the fluorescence of the cooled powder was white, with a *continuous spectrum* in which the thulium lines *were totally suppressed.* In this medium it would seem that thulium is at best a very indifferent activator, with a tendency to be suppressed instead of becoming dominant. (Compare with the observations on europium in Al_2O_3, to follow.)

(2) EUROPIUM

(*a*) *In $NaPO_3$*—A trace of europium added to the bead gave a faint pink luminescence. The spectrum was not easily observable. Under bombardment of cathode rays, however, there was a ruddy glow, and it was possible to note that the spectrum consisted of rather narrow but by no means line-like bands. The crests very roughly were located as shown in table XLV.

(*b*) *In the borax bead* europium gave a rich cherry-red luminescence, under both photo- and cathodo-excitation, with banded spectrum. Bands at 0.625μ and 0.618μ (set A, table XLVI) were dominant.

TABLE XLV—*Bands in the spectrum of europium in solid solution in* $NaPO_3$

μ	$1/\mu\times10^3$	Brightness	Remarks
0.660	1,575	Very, very dim..	
.615	1,626	Bright.....	Belongs to set B, table XLVI
.592	1,689	Dim.....	Belongs to set A, table XLVI
.540	1,852	Bright.....	Belongs to set A, table XLVI

(*c*) *In NaF* a trace of europium gave a bead clear when fused, clouded when cold. The bead glowed a fine pink color during the transformation. It was inert under the Fe spark, but glowed red in the cathode tube. The spectrum showed no narrow bands.

(*d*) *In* CaF_2 (Kahlbaum) there was a ruddy fluorescence with line-like bands throughout the spectrum, those in the red being very bright. Cathode bombardment gave a very complex spectrum of which the components were tentatively located with the hand spectroscope (table XLVI):

TABLE XLVI—*Bands*[1] *in the spectrum of europium in solid solution in* CaF_2

Set A			Set B		
μ	$1/\mu\times10^3$	Δ	μ	$1/\mu\times10^3$	Δ
0.625	1,600		0.650	1,538	
		18= 1×18.00			180=10×18.00
.618	1,618		.582	1,718	
		161= 9×17.89			36= 2×18.00
.562	1,779		.570	1,754	
		163= 9×18.11			108= 6×18.00
.515	1,942		.537	1,862	
		107= 6×17.83			
.487	2,049				
Average interval, set A..... 17.96			Average interval, set B..... 18.00		

[1] The following three bands, which are also present, are probably due to samarium: 0.590 (1,695); 0.550 (1,918), and 0.526 (1,901).

(*e*) *In CaO* (concentration about 1 : 333), after a mild "ignition" in a quartz crucible, europium gives a ruddy fluorescence, both under the iron spark and in the cathode tube. The very brilliant and complex group of exceedingly fine line-like bands were reserved for subsequent detailed study.

(*f*) *In* Al_2O_3 (from alum) prepared by inserting a minute quantity of europium oxalate in a cavity in a mass of the Al_2O_3 and heating to incipient fusion, a line-like spectrum comparable to that in CaF_2, but very dim, was obtained. The bands located are given in table

XLVII. The fluorescence line of the ruby, which is strong in preparations from this sample of aluminum oxide, was very feebly visible, as though partly suppressed by the trace of europium. In consideration of this question, the following experiment is instructive: A splinter from an alundum crucible was dipped into a dilute solution of europium nitrate, and the tip was heated to fusion in an O-H flame. After cooling, the splinter was subjected to cathode bombardment. The result was as unexpected as it was striking. The fused tip glowed red and gave the *ruby spectrum* only. Then followed a dark neutral zone which had not been heated to fusion and was not cathodo-luminescent. Beyond this and very clearly defined was a broad region which glowed strongly under bombardment and showed the spectrum given in table XLVII. The red ruby line was very, very dim.

TABLE XLVII—*Bands in the spectrum of europium in solid solution in* Al_2O_3

Set A			Set B		
μ	$1/\mu\times10^3$	Δ	μ	$1/\mu\times10^3$	Δ
0.551	1,815	72=4×18	0.650	1,538	54=3×18
.530	1,887		.628	1,592	18=1×18
			.621	1,610	54=3×18
			.601	1,664	19=1×18+1
			.594	1,683	

The ruby band of fluorescence at 0.690μ was also very dimly visible. Both sets A and B coincide with sets A and B in table XLVI.

The question of the effect of heat treatment upon the suppression of spectra was further tested by making up samples of europium nitrate in Al_2O_3. These were heated to various temperatures, and it was observed that up to the point of fusion *brightness and definition* increased, but that when complete fusion occurred the *ruby spectrum appeared and the europium bands vanished.*

When, however, a crystal of fluorspar was dipped in the europium solution (in HNO_3) and one corner was heated to fusion, it was in the fused portions that the band spectrum was fully developed and brilliant. Those parts of the crystal which had not been fused glowed but very feebly. Although only one band of those observed in this spectrum and recorded in table XLVII coincides with a band in the spectrum of Eu in CaF_2, the relation between the two is an intimate and remarkable one. As will be seen from the tables, the

interval 18 is common to both spectra, and moreover, the same identical sets A and B occur, and to one or the other of these all the bands belong. In one sense, therefore, the two spectra have an identity. If we imagine set A, *when complete,* to consist of components equally spaced and running through the spectrum with a frequency interval of 18±, and set B to consist of a similar succession

TABLE XLVIII—*Bands in the spectrum of terbium in various solid solutions*

Set	In CaO[a]			In CaF_2[b]			In borax[c]		
	μ	$1/\mu \times 10^3$	Δ	μ	$1/\mu \times 10^3$	Δ	μ	$1/\mu \times 10^3$	Δ
				0.575	1,739				
						31=2×16−1			
	0.565	1,770		.565	1,770				
			16=1×16						
	.560	1,786							
			16=1×16			48= 3×16			
	.555	1,802							
			16=1×16						
	.550	1,818		.550	1,818		0.550	1,818	
A			143=9×16−1						
	.510	1,961				223=14×16−1			
									239=15×16−1
			96=6×16	.490	2,041				
						16= 1×16			
	.486	2,057		.486	2,057		.486	2,057	
			31=2×16−1						
	.479	2,088							
	.608	1,645							
			64= 4×16						
	.585	1,709		.585	1,709				
A′			15= 1×16−1						
	.580	1,724				319=20×16−1	.580	1,724	
			304=19×16						
	.493	2,028		.493	2,028				
			209=13×16+1			209=13×16+1			
	.447	2,237		.447	2,237				
						161=10×16+1			
				.417	2,398				
	.599	1,669		.599	1,669				
						49= 3×16+1			
			176=11×16	.582	1,718				
						127= 8×16−1			
	.542	1,845		.542	1,845		.542	1,845	
			31= 2×16−1						
B	.533	1,876				143= 9×16−1			
			112= 7×16						
	.503	1,988		.503	1,988				
						191=12×16−1			
			305=19×16+1	.459	2,179				
						114= 7×16+2			
	.436	2,293		.436	2,293				

[a] Band at 0.625 due to Eu is omitted.
[b] Bands at 0.630 (Sa), also 0.625 (Eu), 0.594 (Eu), and 0.530 (Eu) are omitted.
[c] Three other lines in borax which are displaced 2 units from set A and are probably components of sets A and B, due to incomplete resolution, are located at 0.622μ, 0.598μ, and 0.494μ.

of components displaced from set A by 7 frequency units, then we can produce the actual spectrum recorded in table XLVI by suppressing all the components in both sets not given in that table, and can pass from table XLVI to table XLVII by suppressing components appearing in the former table and substituting those of table XLVII. Thus, although the spectra may have no bands in common, they are parts of the same system. This is the relationship which has been designated as the *principle of essential identity.*

(3) Terbium

Table XLVIII gives the bands due to the luminescence of terbium in three different solvents. The spectrum of this element in CaO and CaF_2 consists of narrow, line-like bands. In borax glass, where only 7 bands were located, the resolution is somewhat less complete. These spectra afford an excellent example of essential identity, because of the number of bands common to all three. Set A′, which is situated less than 3 frequency units towards the violet from set A, could not be distinguished with certainty from the latter set were the gap much narrower.

(4) Samarium

The luminescence of samarium (table XLIX) still further enforces the principle of essential identity. The interval here is again approximately 16, and we find that the main set for the spectrum of the solution in borax falls in with set A of the spectra of the preparations with CaO and CaF_2. Similarity between these latter solutions here, as in our previous comparisons, might be ascribed to the formation of traces of CaO in the course of the heat treatment of the CaF_2, but this can not be true where *borax-glass* is the solvent and we revert to the proposition already formulated that the location of the *sets* depends only upon the activator and is the same for the various solvents used.

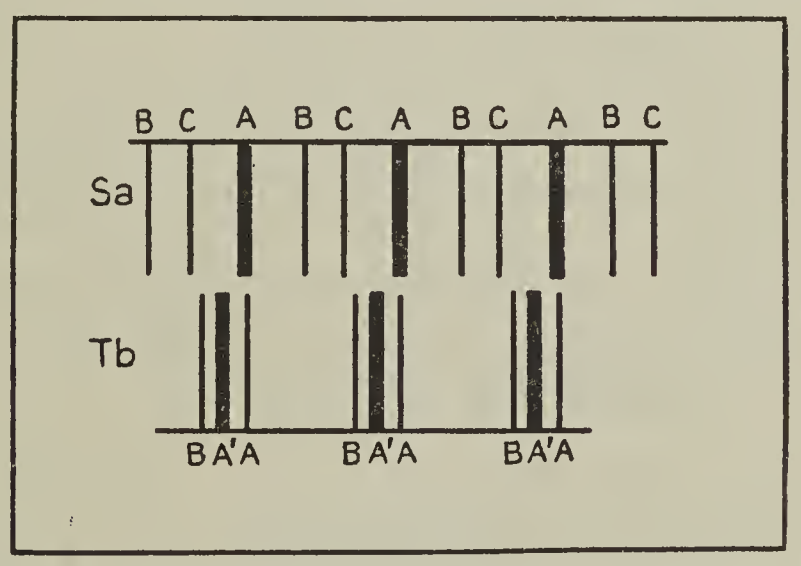


Fig. 64—Rare-earth spectra, grouping of bands in fluorescence of samarium and terbium

Set A in the spectra of samarium and of terbium is practically identical as to location, but the grouping of the other sets with reference to it is altogether different, as will be seen from the diagram in figure 64. This represents the grouping of bands which would occur in a region of the spectrum where all the members of the so-called

sets were represented by actual bands. The spectrum, then, would consist of a system of recurring groups of bands, equidistant and similar. In the samarium spectrum the grouping is symmetrical about set A, with frequency intervals of 6 units to the B and C sets, respectively. Since the group spacing is 16, this gives only 4 units between each group of 3. With this arrangement, 9 out of every 16 bands, provided the distribution were entirely fortuitous, would in general be placed in some set if a departure of one unit on either side of true coincidence were permitted. In the terbium spec-

TABLE XLIX—*Bands in the spectrum of samarium in various solid solutions*

Set	In CaO			In CaF_2			In Borax		
	μ	$1/\mu \times 10^3$	Δ	μ	$1/\mu \times 10^3$	Δ	μ	$1/\mu \times 10^3$	Δ
							0.640	1,563	
	0.580	1,724		0.580	1,724				176 = 11×16
			15 = 1×16−1			15 = 1×16−1			
	.575	1,739		.575	1,739		.575	1,739	
A									31 = 2×16−1
			63 = 4×16−1			63 = 4×16−1	.565	1,770	
									191 = 12×16−1
	.555	1,802		.555	1,802				
							.510	1,961	
	.678	1,475							
			79 = 5×16−1				.650	1,539	
	.644	1,554							
			63 = 4×16−1						
	.618	1,617		.618	1,617				
			64 = 4×16			64 = 4×16			
B	.595	1,681		.595	1,681				
						31 = 2×16−1			
				.584	1,712				
			160 = 10×16			65 = 4×16+1			
				.563	1,777				
	.543	1,841							
	.605	1,653							
			48 = 3×16						
	.588	1,701							
C			63 = 4×16−1						
	.567	1,764							
			64 = 4×16						
	.547	1,828							
				.649	1,541				
	.622	1,607				114 = 7×16+2			
C′							.610	1,639	
				.604	1,655				33 = 2×16+1
						176 = 11×16	.598	1,672	
				.546	1,831				
Eu	.630	1,587		.630	1,587				
lines	.530	1,887					.530	1,887	

trum the three sets are much more closely grouped and the groups are nearly symmetrical about A′ instead of A. Here only 7 out of 16 fortuitously located bands would find a place. The fact that all the observed bands in these spectra have been placed, with very few

departures greater than 1 unit, quite disposes of this question of chance grouping.

GAPS IN THE SETS

The numerous gaps in sets as compared with the positions occupied by visible bands is accounted for in part at least by the methods commonly employed in studying luminescence spectra. The location of bands by the usual process of inspection and setting to the crests or of photographing the spectrum and locating the visible crests in the spectrogram, leads to the detection of only a few of the more prominent bands, while many overlapping and more or less submerged components can not be detected. Thus, where Urbain recorded 11 bands in the spectrum of samarium in CaO, Tanaka,[1] who used the spectrophotometric method previously developed by Nichols and Howes,[2] listed 70 components within the same spectral region. Similarly, Fisher,[3] who photographed the seemingly continuous spectrum of columbium in zinc sulphide and explored the spectrograms thus obtained, finds 32 components which fall into four sets, all having the same interval of 21+.

Every luminescent preparation inevitably contains minute traces of various activators, perhaps much too minute to be detected by any known method of chemical analysis, but quite sufficient to produce luminescence. A. A. Guntz,[4] for example, in his very complete investigation of the luminescence of zinc sulphide, finds that copper is universally present as an activator in that solvent and that no known method suffices to eliminate it. Similarly, it has recently been shown[5] that in NaF uranium produces brilliant luminescence when present in the proportion of $1 : 10^7$ mole fractions. Fortunately, *dominance and suppression* operate to render the study of luminescence spectra less complex, and the principle described as *essential identity* brings into a simple system bands which at first appear to be unrelated.

SUMMARY

Various rare-earth salts were put into solid solution in CaO, CaF_2, Al_2O_3, $NaPO_3$, and NaF, and borax glass.

The photo- and cathodo-luminescence was observed and spectra mapped.

Various cases of the dominance of one activator over others were noted and the conditions studied.

[1] Tanaka. Jour. Opt. Soc. Am., VIII, 287, 1924; also Chapter III of this treatise.

[2] Nichols. Proc. Am. Phil. Soc. LVI 258 (1917); Nichols, Howes, and Wilber. Phys. Rev. (2), XII, 351, 1918; Nichols and Howes. Carnegie Inst. Wash. Pub. No. 298, 1919.

[3] Fisher. See Chapter V of this treatise.

[4] A. A. Guntz. Thesis on the luminescence of sidot blende. Paris, 1924.

[5] Nichols and Slattery. Jour. Opt. Soc. Am., XII, 449-466, 1926; also Chapter V of this treatise.

The line-like bands in the spectra of the solid solutions containing traces of thulium, europium, terbium, and samarium were approximately located and arranged in "sets" having a common and constant frequency-interval. The frequency-interval was found to be 18 (almost exactly) in the case of europium, and 16 for the spectra of thulium, terbium, and samarium. The principle of *essential identity,* first established for the spectra of solid solutions containing uranium, was found to apply to the luminescence of these rare earths, *i. e.,* there are one or more sets of positions in the spectrum which are characteristic of a given activator, and whatever the solvent all the luminescence bands of substances containing the activator in question are so located that their crests coincide with positions in these sets. Spectra thus related are said to be essentially identical, although the particular positions in the set thus occupied may not be the same for the different spectra.

III. THE LAW OF THE OPTIMUM

Upon the basis of the data in section I of this chapter, Professor Merritt[1] has worked out the following theory of the most effective proportion of an activator. It is reprinted here from his recent paper in the *Journal of the Optical Society of America.*

THE RELATION BETWEEN INTENSITY OF FLUORESCENCE AND CONCENTRATION IN SOLID SOLUTIONS

Solid luminescent materials are usually compounds in which a small amount of some active material is intimately associated with a relatively large amount of an inert substance which acts as a solvent or flux. Such compounds are prepared artificially by evaporating to dryness a mixed solution of the two components, or by mixing the components in powder form and then subjecting the mixture to suitable heat treatment. While we have no means of knowing the form in which the active material exists in these preparations, it is generally thought that luminescent materials are to be regarded as solid solutions rather than as chemical compounds.

The variation of brightness with concentration has been studied quantitatively in only a few cases; but it is known that luminescence of considerable intensity may be produced by very minute traces of a suitable active material and that if the concentration is increased beyond a few per cent the brightness is greatly reduced. Maximum brightness is often reached with 1 part of active material to 10,000 of solvent and the optimum concentration is rarely as great as 1 part in 100.

Broadly speaking, the behavior of fluorescent solutions is similar to that of solid luminescent preparations. Fluorescein, for example, which is brilliantly fluorescent in dilute solutions, is almost completely inactive when the solution is concentrated.

The existence of an optimum concentration has been explained by Brüninghaus[2] as the result of absorption. It is assumed that the active material

[1] Merritt. Jour. Opt. Soc. Am. XII, p. 613, 1926.
[2] L. Brüninghaus. Comptes Rendus de l'Acad. des Sciences, 149, p. 1375, 1909.

in the surface layers has for some reason lost its ability to radiate, but retains its power of absorbing the fluorescent light that comes from the interior of the mass. Increase in concentration causes an increase in the fluorescence excited in the interior, presumably in proportion to the number of molecules of the active material; but it also brings about increased absorption of this fluorescent light by the surface layer. The intensity of the light that escapes and is observed is therefore given by an equation of the form

$$I = Kxe^{-kx} \tag{1}$$

where x is the concentration of the active material.

Brüninghaus finds that this equation represents with considerable exactness measurements made on the cathodo-luminescence of manganese in calcium phosphate.

Doubt is thrown on the correctness of the Brüninghaus theory by the fact that the hypothesis on which it is based, which is certainly not true in the case of fluorescent liquids, has received no experimental verification in the case of solids. The equation developed by Brüninghaus fails also to represent the results of the more recent experimental work.

Perrin[1] has suggested two alternative reasons for the decrease in luminescence at higher concentrations:

(1) The exciting light is in the form of quanta of small cross-section, and if two active molecules are so close together that they are struck by the same quant, the energy is divided between the two and is less likely to cause excitation; or (2) when two active molecules are sufficiently close together, their fields overlap and they are coupled in such a way as to diminish their power of responding to excitation.

If the first explanation suggested by Perrin is correct, we should expect the optimum concentration to depend primarily upon the cross-section of the light quant. It would appear likely, therefore, that the optimum concentration would depend upon the wave-length of the exciting light or upon the nature of the solvent. No experimental evidence on these points is available. Several observers have pointed out, however, that the optimum is reached at smaller concentration when light is the exciting agent than when the substance is excited by cathode rays. If we accept Perrin's first suggestion it seems clear, therefore, that the cross-section of a light quant must be greater than the effective cross-section of the electrons in the cathode ray. It appears to me not unlikely that a satisfactory theory based upon the assumption of light quanta of definite cross-section could be developed. Yet the difficulties and uncertainties are considerable, and it seems preferable to attempt first to make Perrin's second suggestion the basis of a quantitative theory.

In the case of liquids the relation between fluorescence and concentration has been investigated by F. Perrin[2] and by Wawilow,[3] each of whom based his theoretical discussion upon the general assumption that fluorescing power is destroyed when two active molecules are close together. For a thin layer of the liquid and large values of the concentration both Perrin and Wawilow find that the intensity of fluorescence is given by an expression of the same form as that proposed by Brüninghaus for solids, and this conclusion is confirmed by the experimental results. But for small concentrations there is complete lack of agreement, both as to the form of the the-

[1] J. Perrin. Ann. de Phys., 11, p. 5, 1919.
[2] F. Perrin. Comptes Rendus de l'Acad. des Sciences, 178, p. 1978, 1924.
[3] S. J. Wawilow. Zsch. für. Physik, 31, p. 750, 1925.

oretical expression for the fluorescence and as to the results of experiment. Both Perrin and Wawilow assume that diffusion of the active material during the period between excitation and reemission is an important factor; in Wawilow's discussion it is the essential factor. In a solid it would seem that the displacement resulting from diffusion, in the extremely short time during which the molecule remains in the excited state, would be so small as to be negligible. In the discussion that follows I have assumed that this is true.

If the optimum concentration is as small as 1 molecule of active material to 1,000 molecules of solvent—and maximum brightness has frequently been found for still smaller concentrations—we must conclude that on the average each active molecule is separated from its nearest neighbor by about 10 molecules of the solvent. It is hard to believe that under such circumstances the two molecules could influence one another to such an extent as to interfere seriously with their excitation. But if the active molecules are distributed at random there will be some whose distance apart is much less than the average distance. And it is clear that the number of molecules that are separated by a given small distance from their nearest neighbor will increase both absolutely and relatively as the concentration is increased.

To put the Perrin suggestion into quantitative form let us assume therefore that if two active molecules are at a distance apart that is less than some distance ρ their luminescence is either completely destroyed or greatly reduced. If we direct our attention to some one molecule A, the probability that another molecule B will *not* lie within the sphere of radius ρ is $(V - v)/V$, where V is the total volume and v the volume of the sphere of radius ρ. The probability that all of the other molecules will lie outside v is $(1 - v/V)^n$, where n is the total number of active molecules. The number of active molecules that are so far apart as to be free to radiate is therefore $n(1 - v/V)^n$. If subjected to some exciting agency each of these undisturbed molecules will radiate and, neglecting absorption, the intensity of luminescence will be

$$I = Fn(1 - v/V)^n$$

It is convenient to take $V = 1$ c. c. and $n =$ the number of active molecules per cubic centimeter. If this change is made,

$$I = Fn(1 - v)^n = Fne^{-rn} \qquad (2)$$

where

$$r = -\log_e (1 - v)$$

With a suitable change in r and F the concentration may be expressed in any convenient form.

It will be noticed that this expression for I has the same form as that proposed by Brüninghaus.

The expression requires modification, however, because of absorption. The exciting light suffers absorption, so that excitation is less intense at points in the interior than at the surface; and the emitted light is in part absorbed on its way out. In each case the absorption is partly due to the solvent and partly to the active material. The latter part of the absorption may be assumed to increase in proportion to the concentration. We must therefore make use of two absorption coefficients, $a + bn$ for the exciting light and $p + qn$ for the emitted light.

In a layer of thickness dy and unit area at a depth y below the surface there are $n(1 - v)^n dy$ active molecules free to radiate and these are subjected to exciting light of intensity $I_o e^{-(a+bn)y}$. If the fluorescence is proportional to the intensity of the exciting light—and such proportionality is confirmed by experiment in all cases where tests have been made—the light

emitted by the layer dy is $Fn(1-v)^n e^{-(a+bn)y}dy$, of which the fraction $e^{-(p+qn)y}$ reaches the surface.

The intensity of the light issuing from the surface is therefore

$$I = \int_0^\infty FI_0\, n\,(1-v)^n\, e^{-(a+bn)y} e^{-(p+qn)y} dy$$

$$= FI_0 \frac{n}{\alpha+\beta n}(1-v)^n = F\frac{n}{\alpha+\beta n}e^{-rn} \qquad (3)$$

where

$$\alpha = a+p \qquad \beta = b+q \qquad r = -\log(1-v)$$

It is assumed that the specimen is so thick that the exciting light is completely absorbed.

Since the concentration is usually given as the ratio of n to N, where N is the number of solvent molecules per cubic centimeter, and since the form of the curve depends only on the ratio of α to β, it is convenient to write the equation in the form

$$I = K\frac{x}{c+x}e^{-kx} \qquad (4)$$

where

$$x = n/N \qquad k = rN = -N\log(1-v), \qquad c = \alpha/\beta$$

Equation (4) may be shown to be consistent with all of the peculiarities in the relation between I and n to which different observers have called attention. For example:

1. It has been pointed out by Urbain[1] that when the luminescence spectrum consists of several bands the optimum concentration is in general different for each. Since the bands occur in different parts of the spectrum, and since in general each band has its own region of excitation, the absorbing power of the mass, both for the exciting light and for the emitted light, will vary, from band to band. In consequence the constant c will have different values and the concentration for maximum I will change.

2. If k is small the exponential term in equation (4) will remain nearly equal to unity until relatively large values of x are reached and for small concentrations the form of the curve will depend chiefly on the value of c. For c small the intensity will therefore rise rapidly to a large value and will then remain nearly independent of x until the exponential factor becomes of importance. Several cases of this kind are on record.

3. Kowalsky and Garnier[2] have found that for a given substance the optimum concentration is smaller for light excitation than for excitation by cathode rays. Samarium in CaS, for example, gave maximum brightness with ultra-violet excitation when the concentration was 1 molecule of samarium to 3,000 molecules of Ca. The same phosphors with cathode ray excitation showed maximum brightness for the preparations containing 1 molecule of samarium to 400 of calcium. This is doubtless the result of the fact that the cathode rays penetrate only a short distance and that their absorption is due almost entirely to collisions with the solvent molecules. For cathodo-luminescence the constant c is therefore large. On the other hand, the solvent is relatively transparent to light. For photo-luminescence c is therefore likely to be small and I reaches its maximum for small values of x. It will be noticed that when c is large equation (4) becomes practically identical with the expression proposed by Brüninghaus.

[1] G. Urbain. Comptes Rendus de l'Acad. des Sciences, 147, p. 1472, 1908.
[2] J. Kowalsky and G. Garnier, Comptes de l'Acad. des Sciences, 145, p. 391, 1907.

TABLE L

Phosphor	K	c	k	s
Uranyl fluorid in sodium fluorid.....	170	0.000005	1.30	3.1
Uranyl fluorid in calcium fluorid.....	202	.00025	.91	2.8
Uranyl phosphate in sodium phosphate.....	165	.0008	.25	1.8

An excellent opportunity for a quantitative test of equation (4) is afforded by the work of Nichols and Slattery,[1] who have determined the intensity of fluorescence as a function of concentration in the case of three different uranium phosphors. In each of the three cases I have determined K, c, and k by trial and have then plotted the observed and computed values of I against x. The results are shown in figures 65, 66, and 67. In each case the curve is plotted from equation (4) while the experimental data are indicated by black circles. The constants K, c, and k for each of the three phosphors are given in table L.

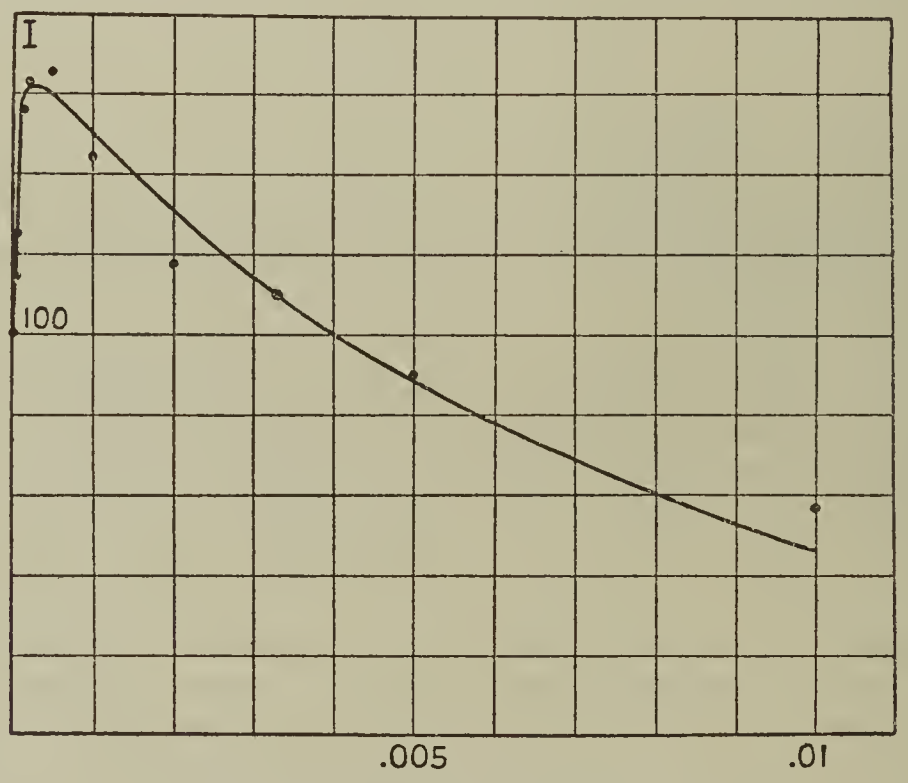


FIG. 65—Uranyl fluoride in sodium fluoride

In the case of uranyl fluorid in sodium fluorid (fig. 65) the optimum concentration, about 0.0002, is smaller than for either of the other phosphors studied. For concentrations lying between 0.00001 and 0.01 the agreement between the observed and computed values of I is as close as could be expected, since the location of the observed points indicates that the experimental errors are of the order of 5 per cent. For concentrations less than 10^{-5} the agreement is less satisfactory. Thus, for $n = 10^{-6}$ the observed value of I is 100, while the computed value is 29. For $n = 10^{-7}$ the two values are 39 and 4 respectively.

In the curve for uranyl fluorid in calcium fluorid (fig. 66) the computed and observed values of I do not in any case differ by more than the experimental errors. In the case of this phosphor the concentration was varied from 0.00012 to 0.0133. In curve B the data for small concentrations have been plotted to a larger scale in order to show the form of the curve in this region more clearly.

[1] Nichols and Slattery. J. O. S. A. and R. S. I., 12, p. 449, 1926. See section I, Chapter VI.

Figure 67 shows the computed curve and the observational data in the case of uranyl phosphate in sodium phosphate. Here also the data for small concentrations have been replotted in curve *B* to a larger scale.

In view of the great difficulty of preparing a suitable series of phosphors, which arises both from the difficulty of obtaining pure materials and from the fact that the heat treatment must be identical for the different mixtures, the agreement between the computed and observed curves seems in all three cases as satisfactory as could be expected.

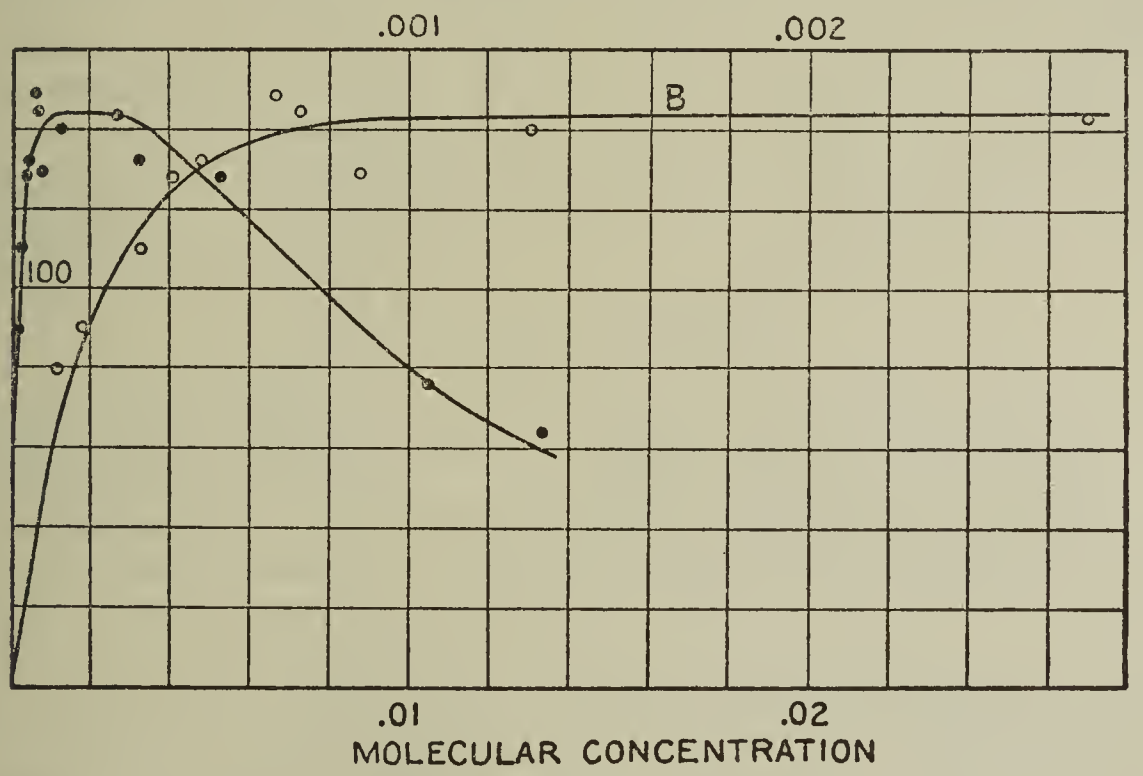


FIG. 66—Uranyl fluoride in calcium fluoride. For Curve *B* the horizontal scale is indicated at the top

The phosphors investigated by Nichols and Slattery are unusual in the fact that the active material is one which is luminescent when pure. In some cases the uranyl salt shows fluorescence when pure that is nearly as bright as is that of the solution at optimum concentration. It would appear that when two molecules of uranium are brought close together their power to fluoresce is not completely destroyed, but only reduced. When the molecules are all crowded together, as in the pure substance, the diminished activity of the individual molecules is offset by the greatly increased number present. If equation (4) is modified to correspond to the assumption of reduced activity, rather than complete destruction of luminescence, when the distance between molecules is less than ρ, the equation takes the form

$$I = K_1 \frac{x}{c + x} e^{-kx} + K_2 \frac{x}{c_1 + x}$$

In the second term a new constant, c_1, takes the place of the constant c of the first term, since it is not to be expected that either the color of the emitted light or the exciting region will be the same when the active molecules are close together. The fluorescence of the uranyl salts in bulk is in fact quite different in color from that of the phosphors studied by Nichols and Slattery. Indeed, we are hardly justified in putting I equal to the sum of two terms, for the tacit assumption has been that both the emitted and exciting light are monochromatic; the application of equation (4) to a phosphor having a broad band can only be justified as a reasonably close approximation. Without developing a more complicated equation—and the lack of experimental data for testing such an equation makes this step unprofitable at the present

time—we can therefore only say that for large concentrations of the uranium salts somewhat brighter fluorescence is to be expected than that computed from equation (4). Inspection of figures 65, 66, and 67 shows that the experimental results are in agreement with this conclusion.

In the case of the phosphate (fig. 67), where the concentration was carried to 0.1, it is to be expected that the difference between the observed and calculated values of I for large values of x will be especially large; and the difference is in fact greater in this case than in either of the other phosphors tested. It is possible that a better value of k would have been obtained by ignoring the observed point at $x=0.1$.

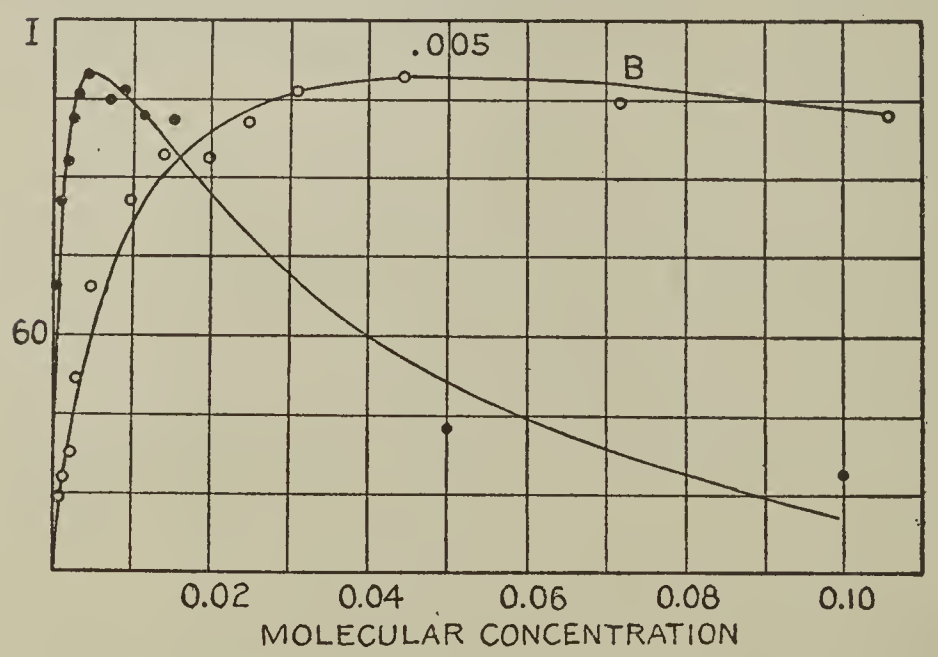


FIG. 67—Uranyl phosphate in sodium phosphate. For Curve B the horizontal scale is indicated at the top

The value of ρ may be computed from the experimentally determined value of k. Since, however, the concentration x has been expressed as the ratio of the number of molecules of the active material to the number of molecules of the solvent, and since also the density of the mass is not known, it will be convenient to express ρ in terms of the average distance between the molecules of the solvent. Assuming a simple cubic lattice, with N molecules of solvent and n of the active material per cubic centimeter, the minimum distance apart of the solvent molecules is $d=N^{-1/3}$ cm. Let $\rho=sd$. Then

$$v = \frac{4}{3}\pi\rho^3 = \frac{4}{3}\pi s^3 N^{-1}$$

Since v is small we may write

$$k = -N \log (1 - v) = Nv = \frac{4}{3}\pi s^3$$

$$s = (3k/4\pi)^{1/3}$$

The values found for s from this equation are given in the last column of table L. The phosphors are arranged in the order of the molecular weights of the solvent. It will be noticed that c increases as we pass to solvents of higher molecular weight, and that s diminishes.

In table L the largest value of s, that for uranyl fluorid, is 3.1. We must conclude, therefore, that when two molecules of uranium are separated from one another by only two molecules of solvent, or are still closer together, they act upon one another in such a way as to reduce greatly their power to fluoresce. That some action of this sort should occur at so small a distance is not improbable. But another interpretation of the results is possible, namely, that if, in the process of mixing the materials of the phosphor, two active molecules are brought within the distance ρ of one another, opportunity is offered by the subsequent heat treatment for them to come still closer, so that a polymerized molecule may be formed, or possibly some chemical combination in which two molecules attach themselves to a single solvent molecule. If this interpretation is correct we should expect that prolonged heat treatment would lead to larger values of ρ and k.

CHAPTER VII

STUDIES OF THE AFTER-GLOW

I. TYPES OF PHOSPHORESCENCE[1]

The existence of phosphorescence of brief duration was long ago revealed by the phosphoroscope of Becquerel. The after-glow of luminescent bodies was studied quantitatively, however, by the earlier workers only when it was of comparatively long duration. Curves of decay were supposed to be all of the same character. It was assumed that the law of diminution of brightness, as expressed by the equation

$$I = \frac{1}{(a_1+b_1t)^2} + \frac{1}{(a_2+b_2t)^2}$$

was of general application and that the phosphorescence of various substances differed only in color, brightness, and duration.

The measurements of Waggoner[2] and of Zeller[3] on phosphorescence of short duration tended to confirm this view. On the other hand, the observations of Ives and Luckeish[4] on the effect of temperature upon the curves of decay of certain phosphorescent sulphides seemed to demand a modification of the usual law in certain cases, while the studies of the phosphorescence of gases by C. C. Trowbridge[5] and of paraffine at liquid-air temperature by Kennard[6] indicated that for the range covered by their measurements the law of decay can not be expressed by a summation of $1/(a + bt)^2$ terms.

In an investigation of the light-excited phosphorescence of the uranyl salts, which, although very brilliant, lasts only for about 0.03 second, Nichols and Howes[7] discovered an entirely new type. This after-glow decays very slowly at first and later very rapidly, whereas, in the cases previously studied, with the exceptions noted in the foregoing paragraph, the opposite is true. Measurements of the luminescence of calcite to be described in section II of the present chapter indicate that this newer form of decay curve is not confined to the uranyl salts.

It is proposed, therefore, to recognize two distinct types of phosphorescence and to designate them as *persistent phosphorescence* and *vanishing phosphorescence*. They are sharply distinguished from one another by the following characteristics:

[1] Nichols and Howes. Proc. Nat. Acad. Sci., IV, 305–312, 1918.
[2] Waggoner. Phys. Rev. (1), XXVII, p. 209, 1908.
[3] Zeller. Phys. Rev. (1), XXXI, p. 367, 1910.
[4] Ives and Luckeish. Astrophys. Jour., Chicago, XXXVI, 1912, p. 330.
[5] C. C. Trowbridge. Phys. Rev., XXXII, p. 129, 1911.
[6] Kennard. Phys. Rev. (2), IV, p. 278, 1914.
[7] Nichols and Howes. Phys. Rev. (2), IX, p. 292, 1917; see also Carnegie Inst. Wash. Pub. No. 298, Chapter IV, p. 38.

Types of phosphorescence—(1) (Characteristic of persistent phosphorescence.) This type has a curve of decay made up of a succession of linear processes, of diminishing slope as we proceed from the origin of time (fig. 68). Three or more such processes have been found in all cases which have been studied through a sufficient range.

(2) (Characteristic of vanishing phosphorescence.) This type has a curve of decay made up of a succession of linear processes, of increasing slope as we proceed from the origin of time (fig. 69).

It is understood that in these specifications and elsewhere, unless otherwise stated, the curve of decay is plotted with time from the close of excitation as abscissæ and the reciprocal of the square root of

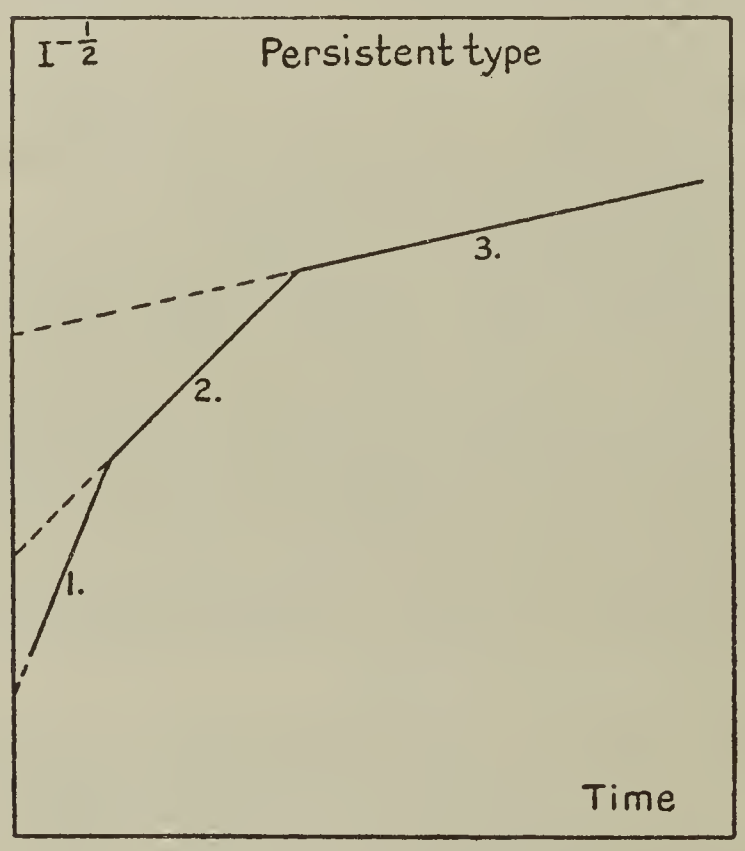


FIG. 68—Curves of decay, persistent type

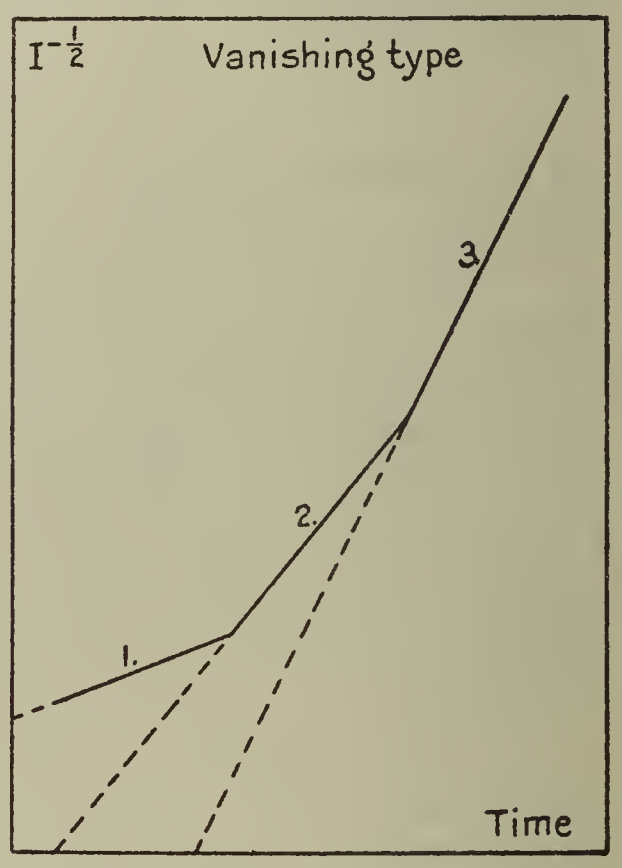


FIG. 69—Curves of decay, vanishing type

intensity ($I^{-½}$) as ordinates. A linear process is any straight portion of the graph, as 1, 2, or 3, in figures 68 and 69. The inference is that the more or less abrupt changes of slope are related to and indicative of real changes in the *processes* by which the emission of light from the phosphorescing body is being maintained.

A distinguishing criterion of type is found in the sign of the intercepts of the various processes at the origin of time. In type 1 the intercepts are all positive; in type 2 the intercepts of processes 2 and 3 are negative.

The passage from one process to the next is presumably never actually discontinuous, as in the above diagrams, but it is sometimes very abrupt, as may be seen in the phosphorescence curves for calcite in section III of this chapter. Sometimes the transition from slope to slope is very gradual, so that the first and second processes tend to

merge into a curved line. It has been shown by the same authors[1] in the case of the uranyl salts that the location of the knees depends on the intensity of the excitation and that distributed knees, so to speak, occur when the exciting light penetrates the crystal and, being absorbed, produces luminescence of decreasing intensity in successive layers; also, that where the conditions are such that excitation is confined chiefly to the surface, the knees are well defined.

Similar modifications of the curve occur in cathodo-excitation, and distributed knees are then probably due to a cathodic discharge containing particles of varying velocity.

Both types may occur in a single substance—Shortly after the completion of our experiments on the vanishing phosphorescence of the uranyl compounds, Misses Wick and McDowell[2] found that some of the same salts, notably $K.UO_2(NO_3)_3$ and $K_2UO_2(NO_3)_4$ when exposed to the cathodic discharge at the temperature of liquid air glowed for many seconds after the close of excitation with decay curves of the persistent type. At $+20°$ the effect is either absent or excessively feeble. Not all the uranyl salts, even among those that are reasonably stable in vacuo, respond to the action of the cathode discharge to a measurable extent.

The Franklin Furnace calcites have the same remarkable property, *i. e.*, vanishing phosphorescence under photo-excitation and persistent phosphorescence under the cathode discharge. Figures 74 and 75 exhibit the vastly different behavior of the same calcite after the close of these two modes of excitation.

Both types of phosphorescence are obtainable with calcite at any temperature between $-180°$ and $+300°$.

Independence of the two types—Since the cathode discharge modifies the surface layers of substances subjected to its action, it might be supposed that calcite crystals after bombardment would show persistent phosphorescence when photo-excited. To test this supposition we placed a crystal of the Franklin Furnace calcite in the bottom of a V-shaped vacuum-tube having a quartz window.

It could thus be excited either by the cathode discharge or from an iron spark. Previous excitation by the cathode rays had no observable effect on the photo-phosphorescence which was of the vanishing type and had, approximately at least, the normal color, brightness, and duration. The photo-phosphorescence could be superimposed upon the persistent cathodo-luminescence, as a fleeting effect, at any time during the life of the latter either after or before the close of the cathodo-excitation. Apparently the two were entirely independent of each other.

[1] Nichols and Howes, l. c.
[2] Wick and McDowell. Phys. Rev., XI, 421-429, 1918.

Misses Wick and McDowell had previously made a similar observation in their study of the cathodo-phosphorescence of the uranyl salts; *i. e.*, that the cathode rays do not render them capable of persistent photo-phosphorescence.

Apparent occurrence of both types with a single source of excitation—Willemite is one of the most brilliant of luminescent substances. The after-glow is commonly fleeting, but masses are occasionally found which exhibit phosphorescence of long duration. Such specimens are persistent under photo-excitation and cathodo-excitation alike. The phosphorescence of the other variety, unlike that of calcite and of the uranyl salts, is of short duration under both kinds of excitation.

The determination of the decay of phosphorescence of a specimen of the latter variety, using the disk phosphoroscope, gave a curve similar to that plotted in figure 69. Processes 1 and 2 are of type 1 (vanishing), but these are followed by a process 3 of lesser slope (fig. 70).

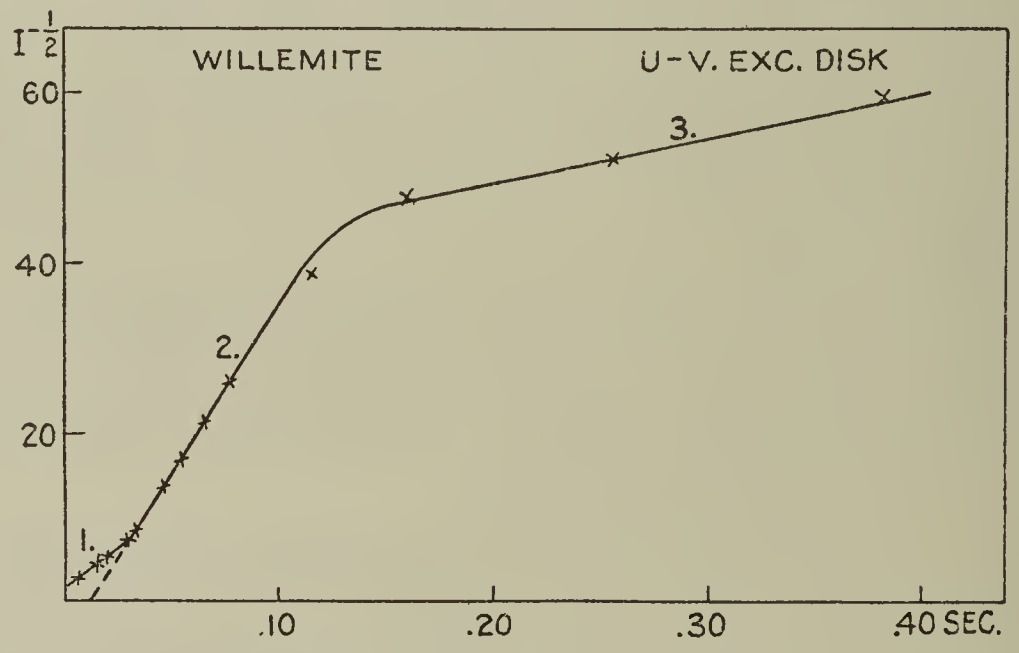


FIG. 70—Curve of decay, willemite

This is obviously a composite curve due to the superposition of phosphorescence of both types. It does not follow, however, that it is a true example of a *single substance* brought to both types of phosphorescence by photo-excitation. The evidence is to the contrary.

(1) The two varieties of willemite are commonly associated. One of our specimens contains parallel veins of the persistent form and of willemite of short duration in the same matrix.

(2) Willemite is associated with the Franklin Furnace calcite.

That the vanishing phosphorescence in the curve in figure 70 may be due to an admixture of calcite is suggested by the following observations:

(*a*) When the disk of the phosphoroscope, coated with the powdered willemite and exposed to the light of the iron spark, was driven rapidly, the region nearest the spark in the direction of revolution, but shielded from the direct light, was a brilliant yellow-green, the regions

approaching the spark, but shielded, were of a dark *blue*-green. This is the effect which would be expected were calcite present, since its red-yellow phosphorescence would give the yellowish cast during the first process of decay, but would vanish before the revolution of the disk was completed.

(*b*) When the collimator of a spectroscope was directed to the rapidly revolving disk the spectrum of the phosphorescent willemite appeared as a broad continuous band extending from the extreme red to the blue. The crest was approximately at 0.54μ and there was suspicion of a weak region in the yellow.

At a somewhat lower speed, which allowed a longer interval of time between excitation and observation, the red end of the spectrum disappeared, and at a much lower speed the yellow and brightest part of the green vanished, leaving a much narrower band in what had been a comparatively feeble region, with its crest in the blue green at about 0.52μ.

The former brilliant crest at 0.54μ was now very dim and lay near the edge of the persistent band. This persistent crest coincides in position with that of the fluorescence spectrum of a willemite of long duration determined spectrophotometrically some years ago.[1]

Obviously we have in this spectrum two, and perhaps three, overlapping bands: a very rapid red band, presumably due to calcite; the band of the willemite of short duration; and a persistent band of small intensity indicative of the presence of willemite of long duration.

Not all specimens of willemite have the complicated curve of decay above described. Waggoner,[2] (1908) in his studies of phosphorescence of short duration, determined the beginnings of the curves of decay of two willemites, one of the rapid and one of the persistent variety. He used the Merritt phosphoroscope having a range up to 0.06 second. His curves are of the persistent type.

Not all phosphorescence of quick decay is of the vanishing type. That the type of phosphorescence is not altogether a question of duration we have abundant evidence. The willemite of quick decay measured by Waggoner is of much shorter measurable duration than the Franklin Furnace calcites, yet its curve of decay is clearly of the opposite type. The same is true of various phosphorescent compounds prepared by Waggoner, *i. e.*, $ZnCl_2$, $CdCl_2$, $CdSO_4$, each with a trace of $MnSO_4$ added, which were heated to redness with a flux of Na_2SiO_4. Although their phosphorescence is of brief duration, they gave decay curves of the persistent type.

There is this distinction between the luminescence of such substances and vanishing phosphorescence. The latter becomes com-

[1] Nichols and Merritt. Phys. Rev. (1), XXVIII, 349, 1909.
[2] Waggoner. Phys. Rev. (1), XXVII, p. 209, 1908.

pletely extinct almost immediately after it ceases to be of measurable intensity; as indicated by the steepness of the second and third processes (fig. 69). In the persistent type of short duration the loss of light during the initial process may go to the very limit of visibility within a few hundredths of a second or less, but if the threshold is not actually crossed the phosphorescence may remain, barely visible in a completely dark room, for a considerable time. Waggoner remarks (on page 216 of his paper): *"It will be noted that in practically all the substances studied, the measurable portion of the decay is over in 0.07 second. Some of the substances, however, may be seen in a dark room for a very much longer time."*

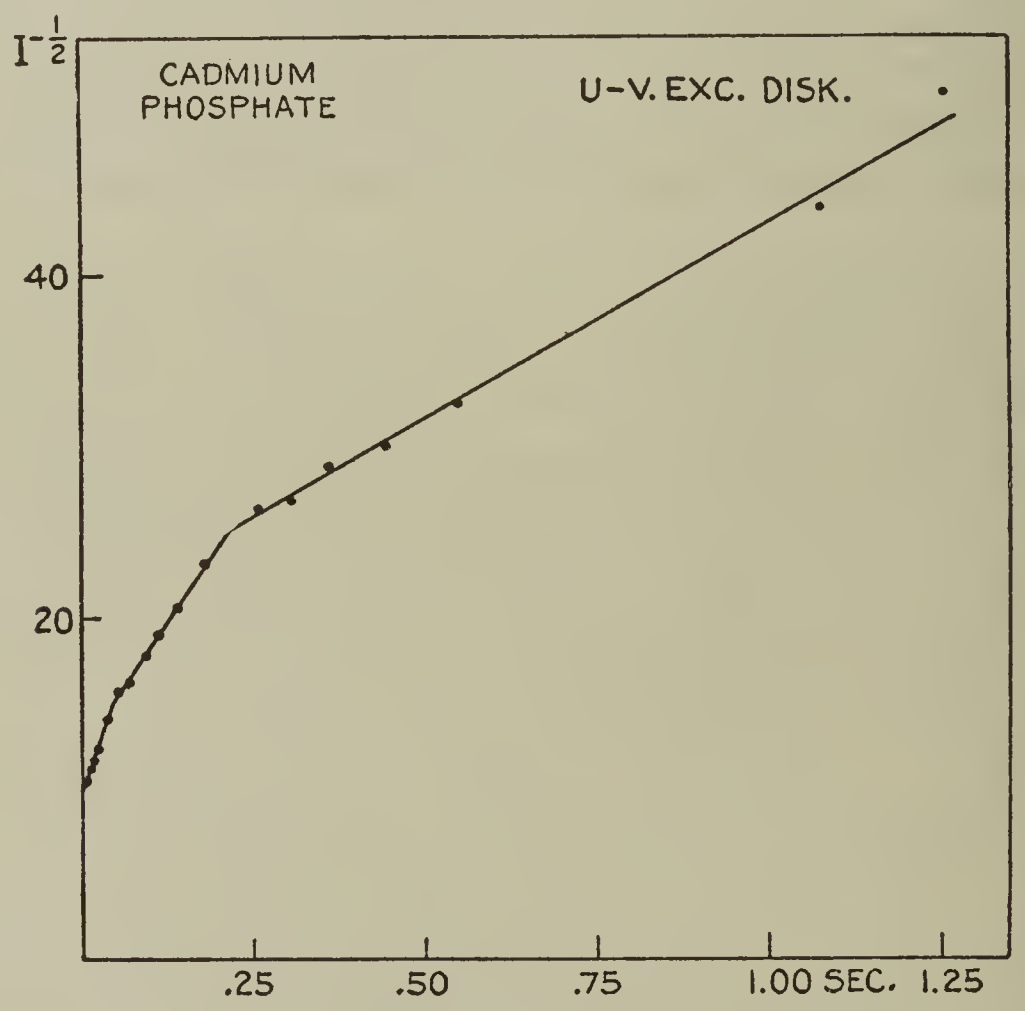


FIG. 71—Curve of decay, cadmium phosphate

Phosphorescence of short duration, when *not* of the vanishing type, may be considered simply as a case of the persistent type in which the rapid initial process reduces the intensity nearly to or beyond the threshold of visibility. The subsequent processes, though gradual, are therefore too faint for observation or invisible. The brightness of the first process may be as great or greater in cases of quick decay than where the phosphorescence continues of measurable intensity for a long time. Zeller,[1] who has studied the beginnings of decay of the phosphorescence of various persistent compounds, has made a note of the fact that duration is not in any simple way related to initial brightness. In a group of phosphorescent cadmium compounds, in particular, some that were too dim for measurement with the phos-

[1] Zeller. Phys. Rev. (1), XXXI, 361, 1913.

phoroscope remained visible for a long time, while those of greatest initial intensity were of very short duration.

An interesting substance which came to our notice during these investigations, through the kindness of Mr. W. L. Lemcke, is a cadmium phosphate prepared by Mr. W. S. Andrews. Under the iron spark it is excited to a fine white phosphorescence having a measurable duration of about 1 second. We determined its curve of decay with the disk phosphoroscope. As may be seen from figure 71, it is of the persistent type and, so far as the white after-glow is concerned, might be classed as of rather short duration; but a very faint ruddy phosphorescence remains for a much longer time. This specimen, as viewed on the rotating disk, is remarkable for the succession of color effects which it exhibits. Pink, very fleeting, is followed by nearly pure white, then for an instant by blue, which goes over into a very persistent pink, turning ruddy as decay progresses.

Such color changes in other substances have been shown to be due to the existence in the phosphorescence spectrum of overlapping bands having different rates of decay, and the striking display would seem to indicate an unusual complexity of composition. We were surprised, therefore, to learn from Mr. Andrews that for the production of this brilliant white phosphorescence cadmium phosphate of exceptional purity is necessary, and that there is no admixture of other metallic salts, as in the preparation of the phosphorescent sulphides. It should not be forgotten, however, in the consideration of such cases as this, that preparations which the chemists would declare to be of the utmost purity may contain activating elements in traces too minute for detection by ordinary analytical processes.

Curves exhibiting the new vanishing type of decay, above described, resemble nothing in the earlier work on phosphorescence so much as the curves obtained as a result of the action of infra-red light on sidot blende. Figure 72 exhibits this phenomenon. Processes 1 and 2 together show the pure decay curve, without infra-red, but if the infra-red is applied after 18 seconds of decay the more rapid process 3–4 ensues. If, however, the infra-red is removed at the end of 25 seconds, the decay resumes a slower rate, as shown by process 5. Processes 1, 3, and 4 taken together show a striking resemblance to the vanishing type of decay. Attempts to hasten the decay of calcite or of the phosphorescent uranyl salts by infra-red action, however, have yielded no result. Here the successively steeper processes must be due to a change in the rate of recombination of the ejected electrons with the active phosphorescing groups. It is commonly believed that only certain groups of particles are active, the majority being considered to be inactive. It is evident that these changes in rate of decay are inherent with the crystal and must be due to a more

or less sudden change in the internal conditions. The electric fields within a crystal are so strong that it is perhaps not surprising that the infra-red field, applied from the outside, can not affect either the phosphorescent action in the active groups or increase the number

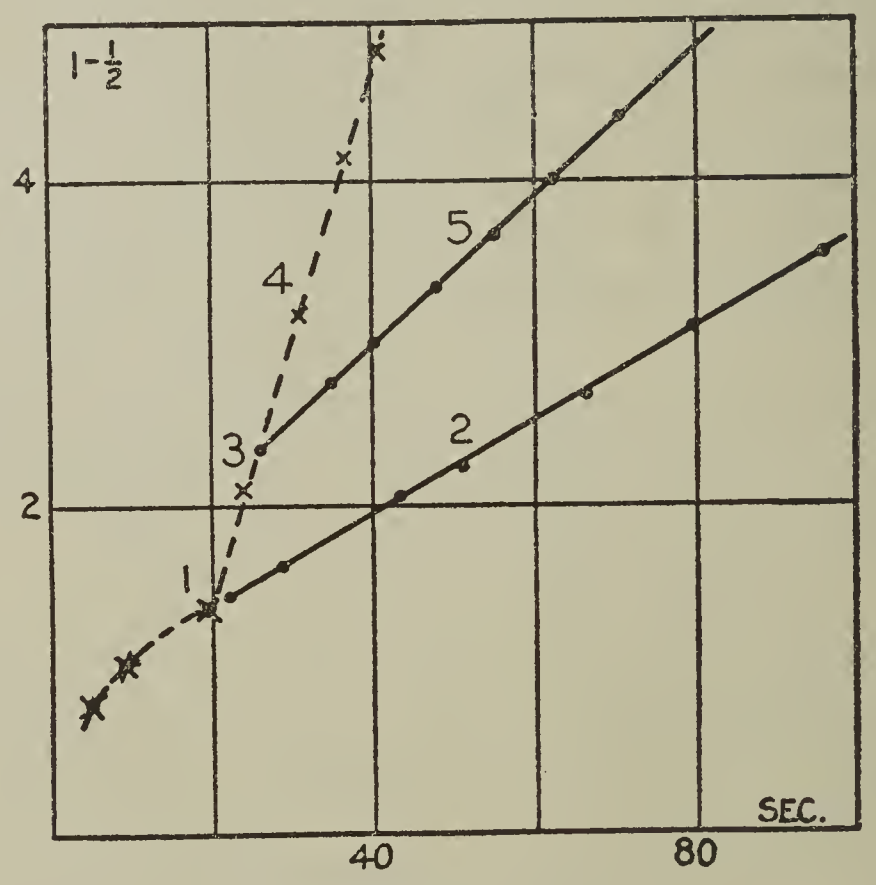


Fig. 72—Effect of infra-red

of free electrons. The sudden change in the rate of decay may be due to a change in the electric field concomitant with the changed orientation of the charged particles, which drives the ejected electrons in greater proportion to the non-active parts of the molecule.

II. THE PHOSPHORESCENCE OF CALCITES

As a part of the investigation of the luminescence of calcite described in Chapter II of this treatise, measurements were made of the rate of decay under various conditions.

AFTER PHOTO-EXCITATION

To determine the curve of decay, a photometer of the form shown in figure 73 was used, where *C* is the comparison lamp movable along a bar, *LB* is the Lummer-Brodhun cube through which a region on the rim of the drum of the disk phosphoroscope (briefly mentioned in Chapter II) was viewed by the eye at *E*.

A light-filter, *F*, was interposed between the comparison lamp *C* and the Lummer-Brodhun cube. Before taking measurements, however, elaborate screening was employed to exclude stray light coming from the exciting source.

The usual method was to maintain a constant angle as above between points of excitation and of observations, varying the speed of

the motor for successive settings. An assistant would adjust the motor speed, then move the comparison lamp along the bar until the observer announced a match. He would then immediately read the speed from the galvanometer scale which was mounted above the bar, and subsequently read the photometer setting. Thus the observer's eyes were spared, which is an important precaution in the readings at low speeds for which the brightness drops to less than 1/1,000 of the initial brightness. Occasional interchanges between observer and assistant in these experiments tended to eliminate the bias of both and check the results.

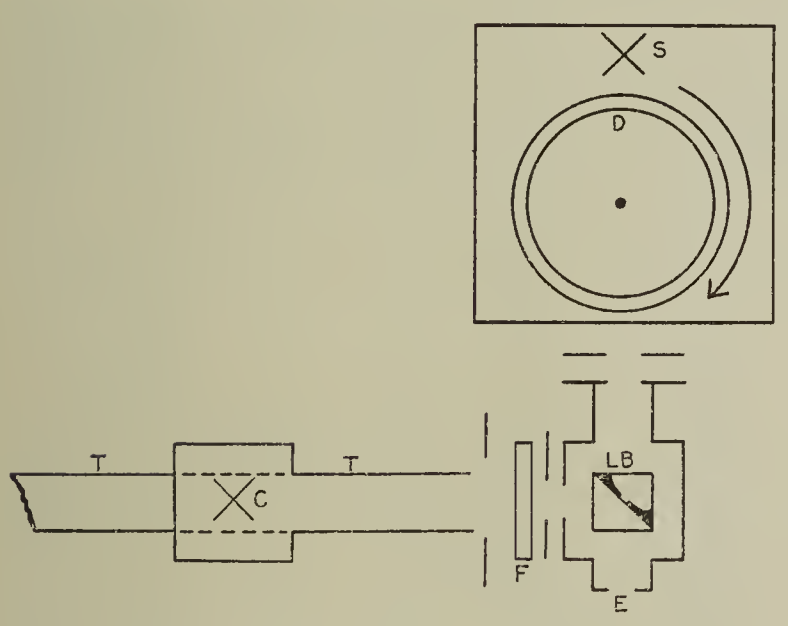


FIG. 73—The disk photometer

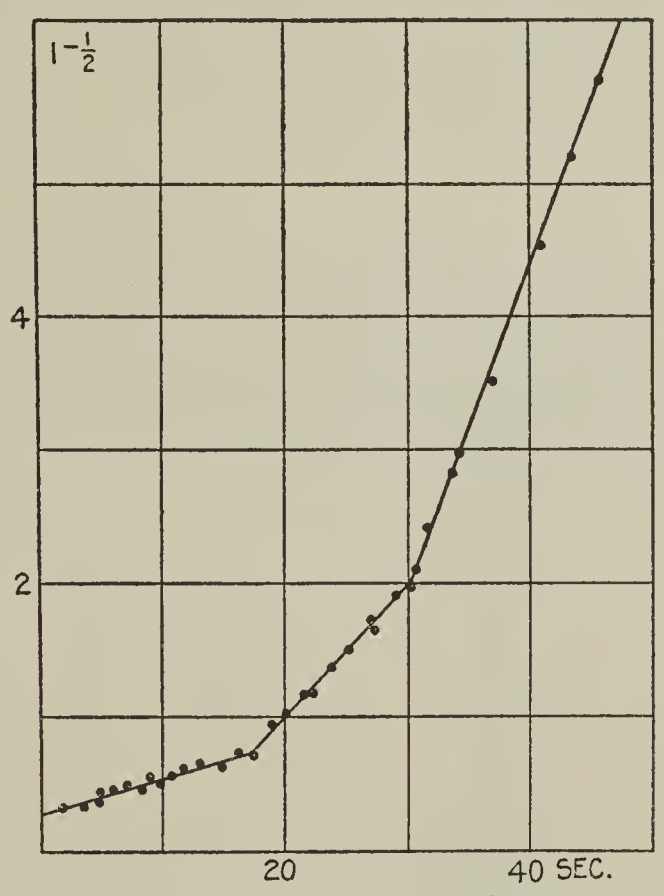


FIG. 74—Decay of phosphorescence after ultra-violet excitation (calcite)

The curves thus obtained were of the form shown in figure 74. Plotted with the reciprocal of the square root of density as ordinates they indicate three successive linear processes with increasing rates of decay, a type previously supposed to be peculiar to the phosphorescence of the uranyl salts.

In the use of the disk photometer, as with any method in which periodically repeated exposures in excitation occur, results are comparable only throughout the range of speeds for which saturation is obtained. For the calcite under observation and with the intensity of excitation available, saturation was found to exist for all speeds of the disk less than that corresponding to 0.02 second decay. Measurements in which the time-interval from the close of excitation was not greater than 0.02 second were accordingly rejected.

Curves of the type shown in figure 74 differ so fundamentally from those universally associated with phosphorescence that one is

at first inclined to question their validity and to ascribe their form to the methods necessarily employed in the study of phosphorescence of short duration. The authors went into this question very carefully in their investigation of the photo-phosphorescence of the uranyl salts, already cited, and convinced themselves by varying the form of the apparatus and the mode of excitation that the new curves were correct. In the discussion of types of phosphorescence in section I of the present chapter they indicated certain fundamental distinctions between the curves of decay of persistent phosphorescence and those characteristic of vanishing phosphorescence and showed that the latter can not be regarded as the first stages of curves of persistent phosphorescence. There is, indeed, good reason to believe that we have in the two cases distinctly different effects.

CATHODO-LUMINESCENCE.

To determine the law of decay of the phosphorescence produced by cathode rays, a crystal, *P*, was placed in the bottom of a V-shaped vacuum-tube (see fig. 10 in Chapter II) and was viewed directly through the transmitting zone of the Lummer-Brodhun cube of the

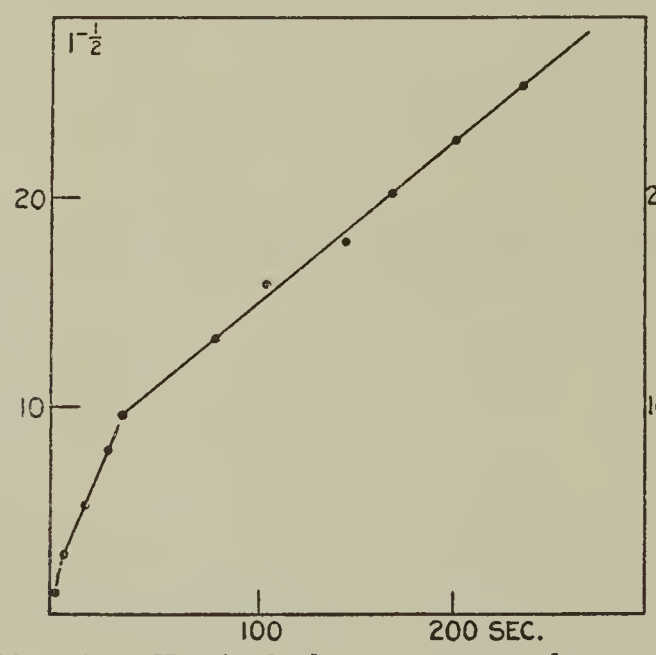


FIG. 75—Typical decay curve, sharp knee, calcite

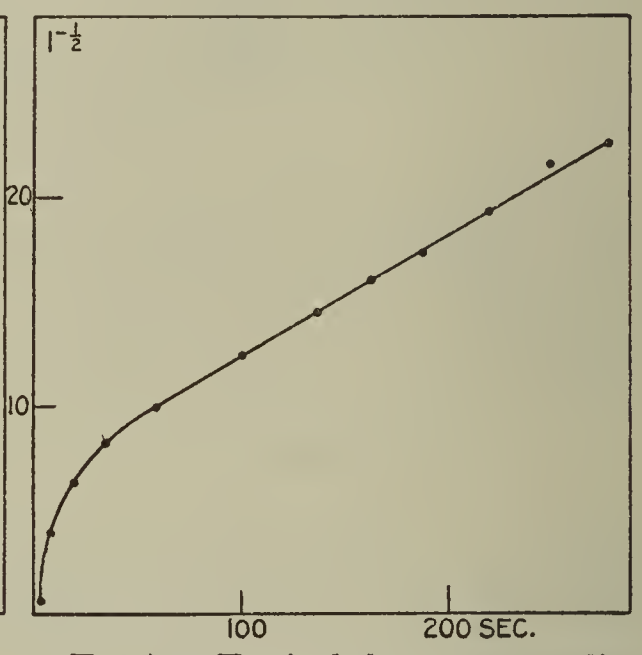


FIG. 76—Typical decay curve, distributed knee, calcite

photometer. The comparison light for the reflecting zone was transmitted through a screen of ground glass or milk glass from a small tungsten lamp mounted upon a long photometer bar. The approximate color match was obtained by the use of a suitable orange-yellow color-screen. The excitation was produced by means of a large motor-driven influence machine.

The time of close of excitation was automatically recorded on a chronograph; the subsequent times when the brightness of phosphorescence matched that of the comparison light placed at previously selected stations along the bar was indicated upon the same chronograph sheet by tapping a key in the chronograph circuit. The first observation was made as soon as practicable, *i. e.*, about 0.4 second

after the close of excitation and readings were continued for about 300 seconds. The range of intensities was so great that the farther end of the bar was reached some time before the run was completed and the subsequent observations were obtained by substituting the milk-glass screen for that of ground glass. The ratio of transmission of the two, which was about 1 : 80, was carefully measured.

The curve in figure 75 is characteristic of the cathodo-phosphorescence of these calcites, but as in the case of the curves of decay of the persistent phosphorescence of other substances, the first two linear processes tend to merge, giving curves of the form shown in figure 76. This occurs, as has been pointed out on a previous page, whenever

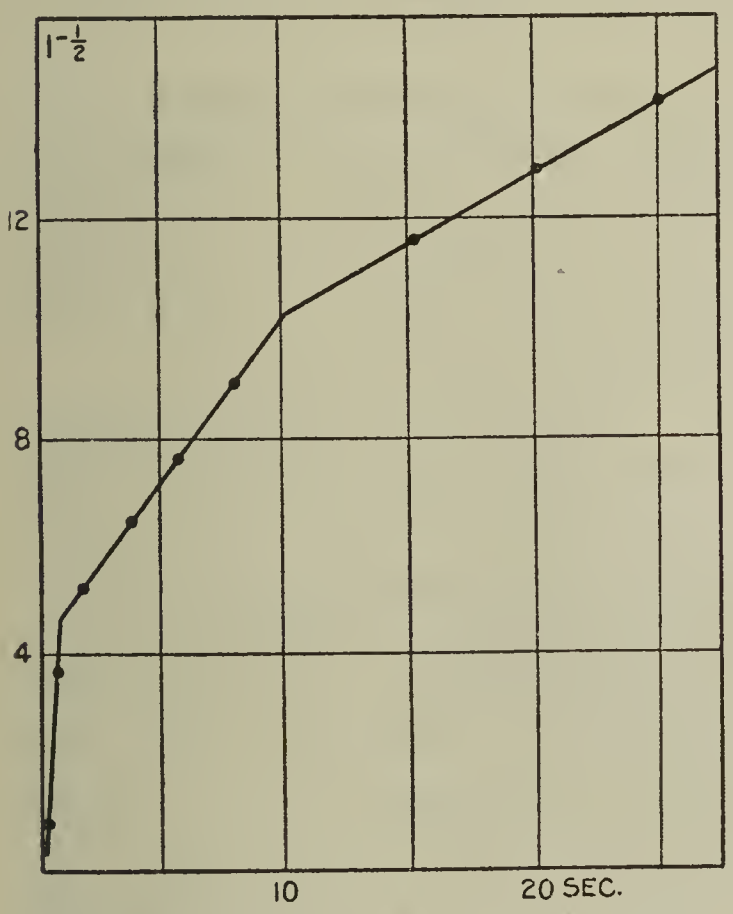


FIG. 77—Cathodo-excitation of calcite. Three processes

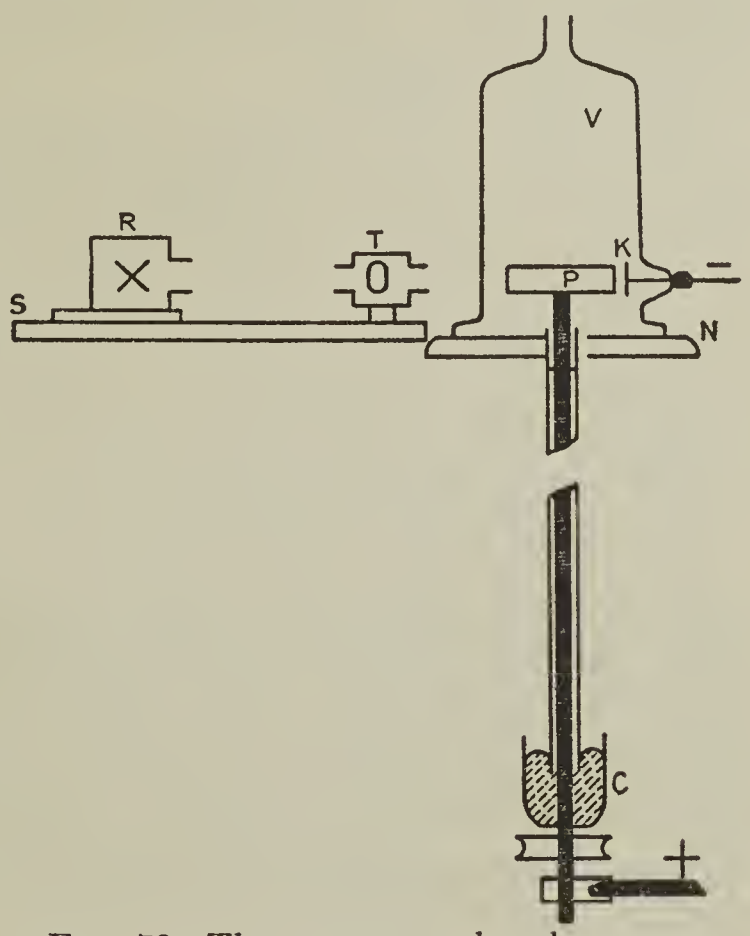


FIG. 78—The vacuum phosphoroscope

various portions of the substances are subjected to excitation of widely different intensity.

In photo-luminescence this is due to the penetration of the exciting light to the inner layers of a crystal; in the case of cathodo bombardment it may also be due in part to the existence in the cathode stream of particles having different velocities. It appeared that the colored film on the surface of calcite, due to prolonged exposure to cathode rays, was conducive to the type of curve in figure 76, whereas the simpler form with well-defined knees was characteristic of crystals with fresh unmodified surfaces.

Shorter runs in which the stations along the bar were placed nearer together, allowing just sufficient time to make the successive observations, served to establish more conclusively the linear character of

the earlier processes. Figure 77 gives the results of such a run. The initial observation in this and in the two preceding curves is located at the origin of the time ordinate. Such readings were made before the close of excitation. The initial position is such as to indicate even more rapid decay of phosphorescence during the first half second than subsequently, but, by this method, it was impossible to obtain readings lying within this interval.

Since the whole of the visible processes of decay in the case of the *photo-phosphorescence* of these calcites occurs during this first half second of time, it was deemed of interest to determine, if possible, what takes place during this interval when the excitation is by cathode bombardment. To this end we constructed a phosphoroscope capable of running in vacuo.

The disk, which was 4.2 cm. in diameter and which carried a flat periphery as in the instrument already described, was mounted at the upper end of a vertical steel shaft 115 cm. in length. This passed coaxially through an iron tube 1.3 cm. in diameter. At the upper end this tube was threaded with a circular iron plate, N (see fig. 78), upon which a vacuum-tube, V, with flanged lip was mounted.

The cathode K was in a side tube. It faced the periphery of the disk at a distance of about 0.5 cm. The iron plate served as anode.

The iron tube within which the steel shaft revolved was provided with a deep iron cup, C, at the bottom, like the cistern of a barometer, and the shaft passed through a mercury-tight stuffing-box in the base of this cistern. The shaft was motor driven at various speeds from pulleys attached below the stuffing-box. When the cistern was filled with mercury and the vacuum-tube exhausted with a Gaede pump, the mercury rose around the shaft, as in a barometer-tube, and a good cathode-ray discharge was readily obtained and maintained. By means of countershafts and reduction gears, the speed of the disk could be varied from twenty or more revolutions a second to one revolution in one hundred seconds.

The intensity of the phosphorescence was measured by reading the position of the comparison lamp R on the bar S when the two fields were of equal intensity in photometer T. The range of the measurements made with this instrument is so great that they can not adequately be represented in a single diagram. Indeed, it was not found advantageous to make a detailed and continuous study of the entire range upon a single specimen, because calcite, which is one of the most stable of luminescent substances under photo-excitation, becomes rapidly fatigued when exposed to cathode rays, with permanent discoloration of the surface layers.

Three sets of experiments were therefore made, using freshly prepared coatings of the powdered crystals:

(1) *From 0.06 second to 0.60 second*—A typical curve for this range is shown in figure 79. The whole of this curve lies within the time-interval between the close of excitation and the first observation made by the method of single excitation already described.

Like the curve for the vanishing phosphorescence produced by photo-excitation (fig. 74), it is made up of sharply separated linear processes, but of the opposite type (*i. e.*, that usually associated with persistent phosphorescence).

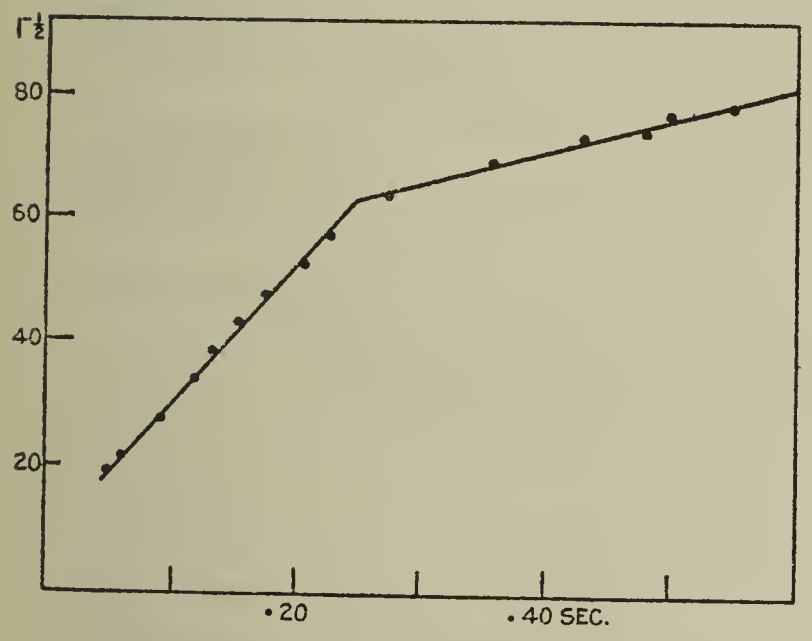


FIG. 79—Calcite in the vacuum phosphoroscope (.60 sec.)

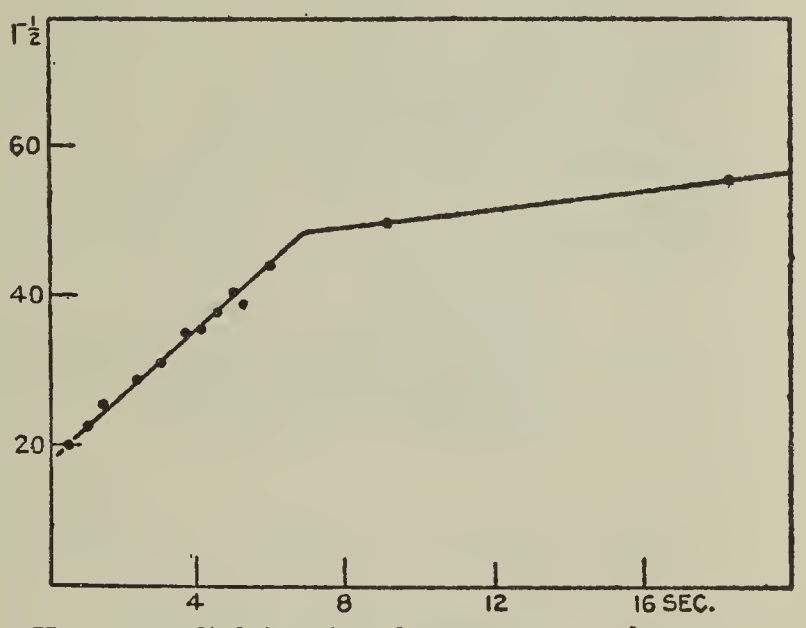


FIG. 80—Calcite in the vacuum phosphoroscope (20 sec.)

It is clear, therefore, that so far as the law of decay is concerned the beginnings of persistent phosphorescence are *not* like the curves for vanishing phosphorescence. It is also evident that the *first process observable by the method of single excitation is not the initial process* in the case of persistent phosphorescence, but is preceded by an earlier and more rapid decay lasting less than half a second.

(2) *From 0.60 second to 20 seconds*—This interval corresponds approximately to that covered by figure 80. Like the curves which had been obtained over this interval of time by the method of single excitation, those resulting from measurements with the revolving disk in vacuo are characterized by a well-defined knee at about 7 seconds, separating two linear processes. The results of the two methods are identical as to type, as may be seen by comparing figure 80 with figure 77.

(3) *From 0.6 second to 300 seconds*—For this great range the difficulties of maintaining a constant vacuum and cathode discharge were such that the authors contented themselves with establishing the existence of a knee in the curve at about 40 seconds corresponding to that obtained by the method of single excitation (fig. 75) and of a linear process beyond.

III. THE EFFECT OF HEAT TREATMENT UPON THE CATHODO-PHOSPHORESCENCE OF FLUORITE

[Describing experiments by Frances G. Wick and Josephine M. Gleason.][1]

During the study of the cathodo-luminescence of fluorites described in Chapter V, section III,[2] changes in the phosphorescence were observed that led to the work to be described here, in which observations were made to determine the way in which the phosphorescence excited by cathode rays is changed by heating the specimens before excitation. A study of the effect of previous excitation and of variation in the duration of bombardment are also included.

The specimens of fluorite, containing various rare earths, used for this work were those employed in the spectroscopic study discussed in Chapter V and are designated by the same numbers, viz,

Specimen 1. Blue-green fluorite from Weardale, England.
Specimen 2. Purple fluorite from Weardale, England.
Specimen 3. Yellow fluorite from Scoredale, England.
Specimen 5. Chlorophane from Virginia.

PROCEDURE

The method of studying the decay of phosphorescence excited in these specimens by cathode rays is one which has been commonly used. The specimen, placed in a cathode-ray tube in such a position that the rays struck it at an angle of about 45°, was excited by the discharge from a Wappler machine at varying voltages, corresponding to an equivalent spark-gap of from less than 1 cm. to 2 cm. Since the specimens gave off gas upon bombardment, it was necessary to keep the oil-pump, which was used for exhausting the tube, running all the time. The arrangement of apparatus used to study the decay is shown in figure 81. A Lummer-Brodhun cube, *A*, was

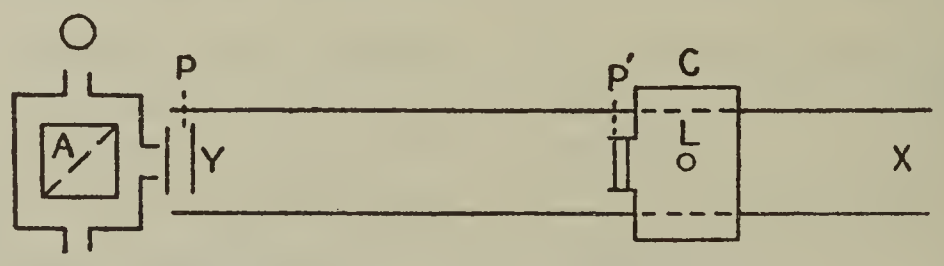


FIG. 81—Photometer arrangement

placed at one end of a track, *XY*, about 3½ meters long, and the specimen in the cathode-ray tube was placed opposite one face of the cube. The comparison source *L*, a tungsten lamp of low voltage, was mounted on a carriage, *C*, running on the track, on which, at intervals of 25 cm., stops were placed. Colored and ground-glass absorption plates, *P*, *P'*, were inserted to obtain a comparison light of proper color and intensity. A chronograph was used for the

[1] F. G. Wick and J. M. Gleason. Jour. Opt. Soc. Am., IX, p. 639, 1924.
[2] See also F. G. Wick. Phys. Rev. (2), XXIV, p. 272.

measurement of time, starting when the cathode-ray bombardment was stopped by breaking the primary circuit of the transformer of the Wappler machine. The time was again recorded when the intensity of the specimen *B* matched that of the comparison *L* in its nearest position. The carriage was then moved to the next stop and allowed to remain until a match was obtained, and this procedure was continued until the phosphorescence was too faint to observe.

After the phosphorescence of the natural material had been observed in this way, curves were obtained from pieces of the same specimens subjected to various forms of heat treatment. The material was placed in a muffle resistance-furnace and gradually heated up to temperatures as high as 600° C. In general, the effect of heating was to remove all color from the natural fluorite and to change the color of the cathodo-luminescence, usually adding to the original green or blue a small component of red. The period of phosphorescence was, for most fluorites, longer after heating, although there were several exceptions to this rule. The effect of repeatedly bombarding the specimens was observed, and a comparison was made of the curves observed with the same specimen following excitations of different lengths.

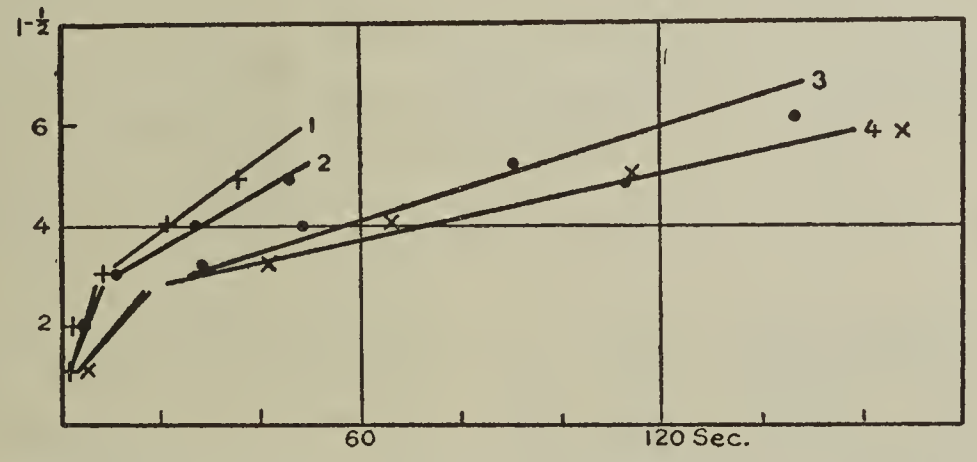


FIG. 82—Specimen 2. Decay curves showing effect of heating and repeated exposure to cathode rays

Figure 82 shows the results obtained from specimen 2. Curves 1 and 2 are decay curves of the natural crystal taken after two consecutive exposures to cathode rays. Curves 3 and 4 are corresponding curves taken after the specimen had been heated for 2½ hours, reaching a maximum temperature of 400° C.

It will be observed that these curves are all of the usual type for long-period phosphorescence, consisting of two linear processes, the first of which is the more rapid. A comparison of curves 1 and 2 with 3 and 4 shows that the heating before bombardment increases the duration of phosphorescence and makes the rate of decay slower. Comparison of 1 with 2 and of 3 with 4 shows that the rate of decay is slower after the second bombardment in each case than after the first. This is the effect usually observed in phosphorescent materials,

and indicates that there is a building up of the phosphorescence by repetition of excitation, due to some secondary change that persists after the phosphorescence has disappeared.

Figure 83 shows the effect of continued repetition of excitation of natural and heated samples of specimen 3. It will be observed that the duration of phosphorescence in the heated material, curves *A* to *C*, is much greater than in the natural specimen, curves 1 to 7, although the exposure was only half as long. The lengthening of the period upon repeated exposure continues up to a certain point, depending upon the duration of excitation and the interval, then a state of saturation is reached beyond which further exposure produces no change in the curve. Figure 84 shows such saturation in specimen 3 after a number of exposures of 10 seconds each.

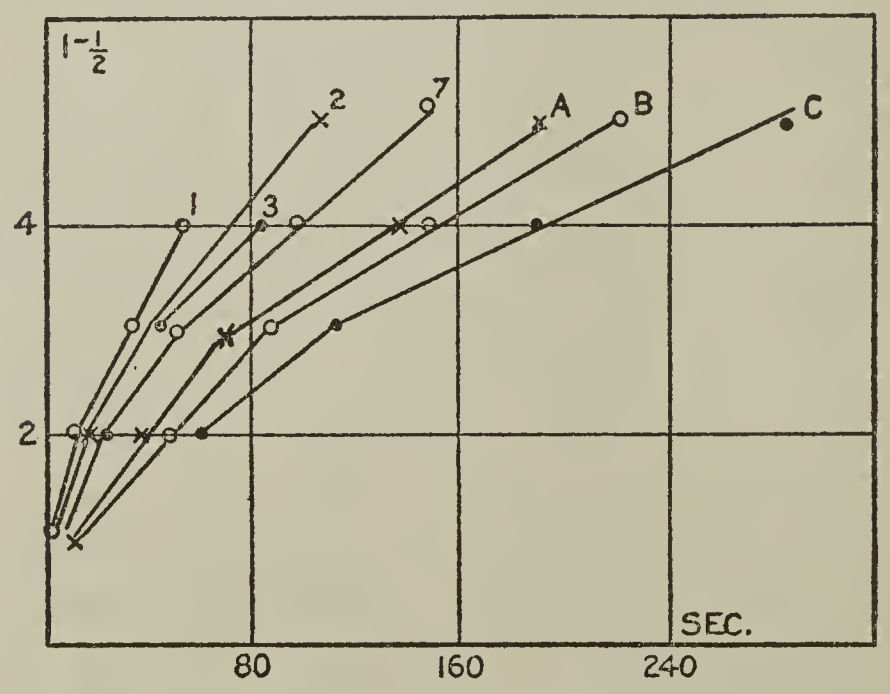


FIG. 83—Specimen 3. Curves showing effect of repeated exposure

1, 2, 3, 7, unheated specimen (curves between 3 and 7 omitted); exposures, 30 seconds; interval between exposures, 150 seconds.

A, B, C, specimen previously heated to 400° C. for 2 hours; exposures, 15 seconds; intervals 300 seconds.

Figure 85 shows the effect produced by varying the period of excitation. The longer exposure was made first and the specimen rested over night before the shorter exposure was made. As is to be expected, the longer exposure is followed by the longer period of decay.

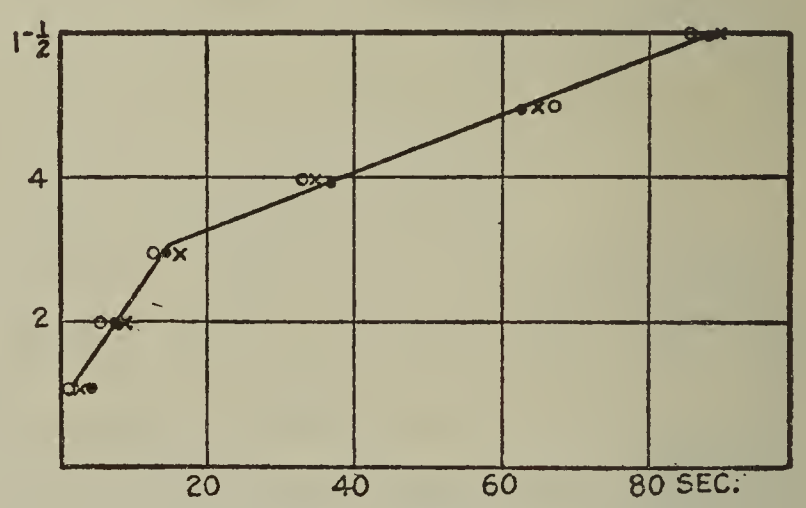


FIG. 84—Specimen 3. Saturation produced by repeated exposures of 10 seconds each

Identical curves due to three exposures preceded by others

FUSED SPECIMENS

Specimens of fluorite fused by playing over their surface an oxyhydrogen flame and subsequently heated in an ordinary blast were found to acquire optical properties radically different from those observed in the unfused state,[1] changes probably due to oxidation of

[1] F. G. Wick. Phys. Rev., (2) XXIV, p. 272, 1924.

the surface. The phosphorescence color of the material in the oxidized state was usually red or yellowish instead of the blue or green of the natural specimens. A study of the phosphorescence of this oxidized material proved to be of special interest, because the effect of repeated bombardment was found to be opposite to that observed in natural fluorite and in many other substances.

When a freshly fused sample of specimen 2 was bombarded repeatedly, the period of decay was made shorter by each succeeding excitation, as shown in figure 86. Sufficient repetition of bombardment brings about a condition of saturation, after which no change is produced by repeated bombardment, as is shown in figure 87.

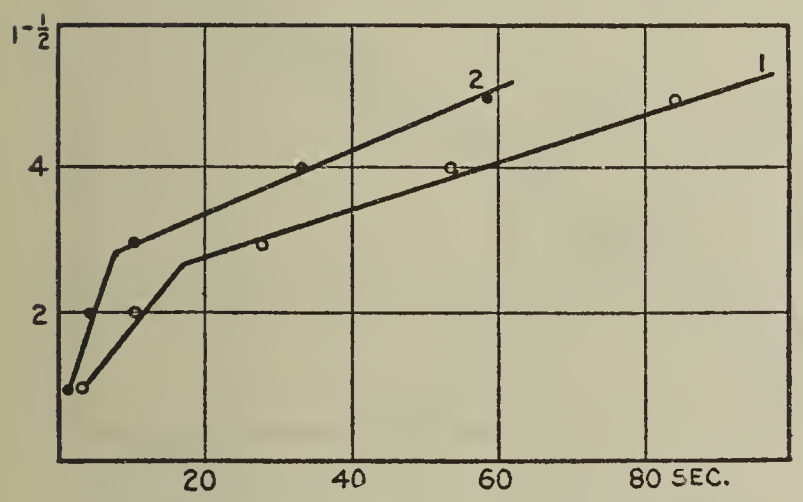


FIG. 85—Specimen 2. Effect of length of exposure on heated specimen

1, exposure 15 seconds. *2*, exposure 6 seconds

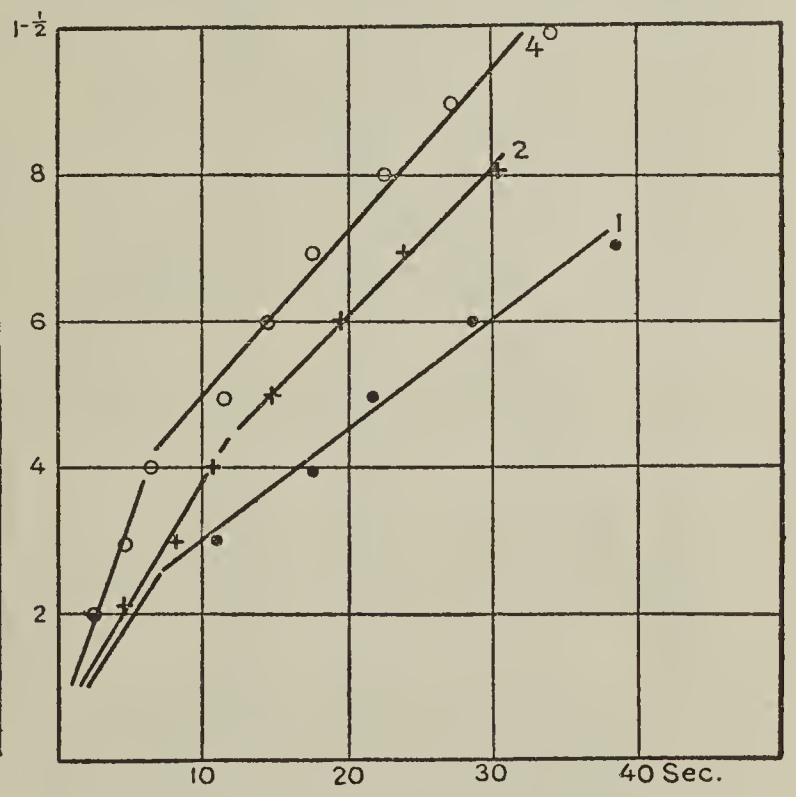


FIG. 86—Specimen 2, after fusion in oxy-hydrogen flame

Exposures of 1, 2, and 4 were 5, 10, and 30 seconds. Interval between 1 and 2, 180 seconds; between 2 and 4, 215 seconds. An exposure of 12 seconds was made between 2 and 4

Figure 88 shows a series of decay curves for the same specimen after it had rested for 24 hours. The effect of repeated excitation is in the same direction as for the freshly fused specimen, but less pronounced.

Many observations made on fused samples of specimen 1 brought out the same points as those observed with specimen 2. A typical set of curves is shown in figure 89. It will be observed that the period after the second exposure is slightly longer than that after the first, conforming with results usually obtained, but the period is shortened by subsequent bombardments, as in the case of specimen 2. This shortening of period with repeated bombardment was found repeatedly in a number of sets of observations upon both specimen 1 and specimen 2.

DISCUSSION OF RESULTS

The difference in behavior of the natural and fused specimens is very striking in that the period of the one increases under the same treatment which causes that of the other to decrease. One possible explanation is that the fused specimens are very sensitive to temperature changes and become more conducting with the rise in temperature which takes place under cathode bombardment. Natural fluorite, which shows an increase of period upon repetition of bombardment, is not sensitive to temperature change and the effect of an excitation persists. It is thought that increase in conductivity of phosphores-

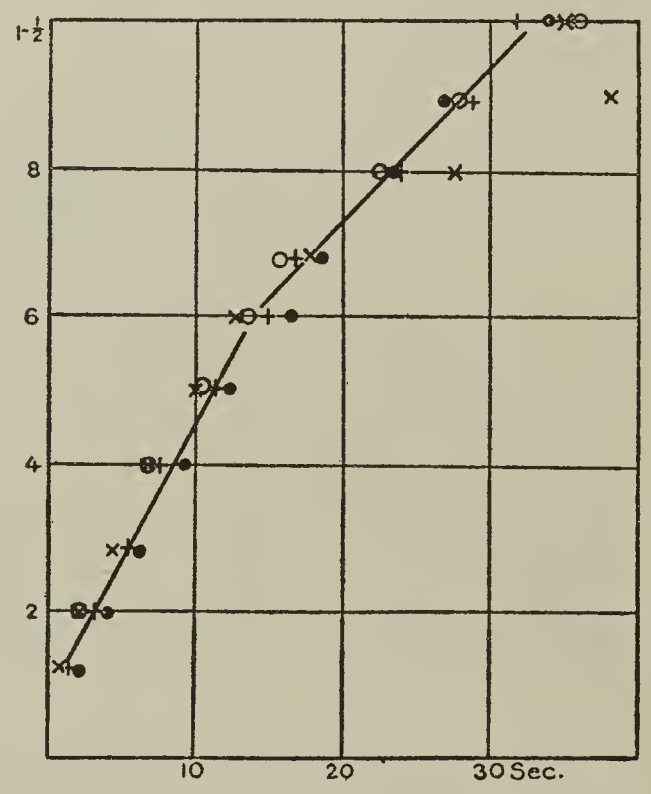


FIG. 87—Specimen 2, fused, same as for fig. 86, 10 min. later

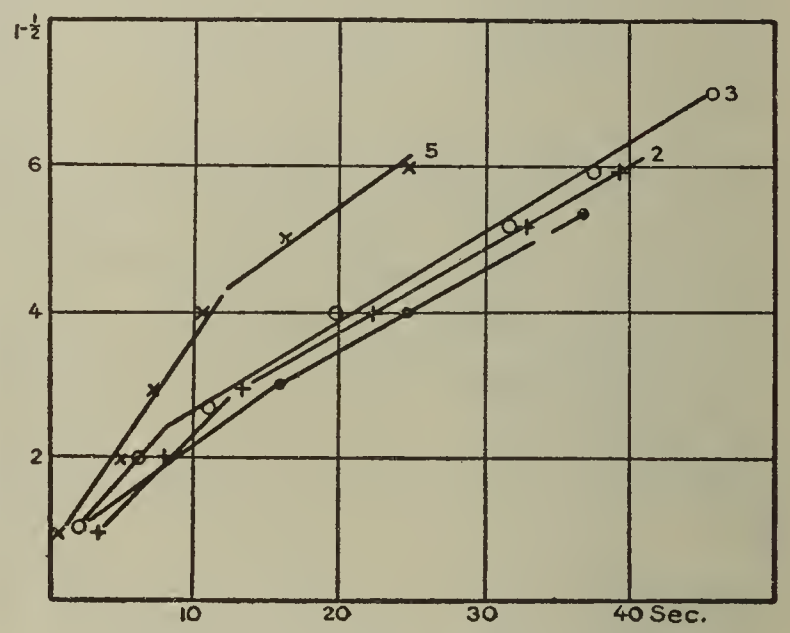


FIG. 88—Specimen 2, fused, same as for figures 86 and 87, 24 hours later

Exposures for 1, 2, 3, and 5 were 5, 10, 20, and 60 seconds. Intervals 83, 98, 140 seconds

cent material shortens the period of decay by facilitating the return to the normal condition of electrons displaced during excitation. An increase of conductivity of the fused material may shorten the period more than the stimulus from previous excitations tends to lengthen it. This would explain such results as those shown in figures 86, 88, and 89. The lengthening of the period after the second bombardment shown in figure 89 may be explained by assuming that the rise in temperature after the first excitation was not sufficient to counteract the persistent effect of the bombardment. After succeeding bombardments the period was reduced by rise in temperature to such an extent that any tendency to increase due to bombardment was counteracted.

It has been observed that clear, perfectly formed crystals have a shorter period of phosphorescence than the more opaque and less

perfect specimens. Pulverizing the specimens was observed to increase the period, and the process of heating previous to bombardment which lengthens the period usually leaves the specimen cracked and opaque. These effects may also be explained by assuming that the conductivity of the perfect crystals is higher than that of irregular masses.

A possible factor in the explanation of the difference in the response of the fused and the unfused specimens to cathode rays is the fact that the oxidized specimens used were thinner and only the surface is excited to luminescence, while, in the case of the natural crystals, the light extends throughout the crystal and can be seen from a side of the specimen not directly bombarded. Since the crystal is not a

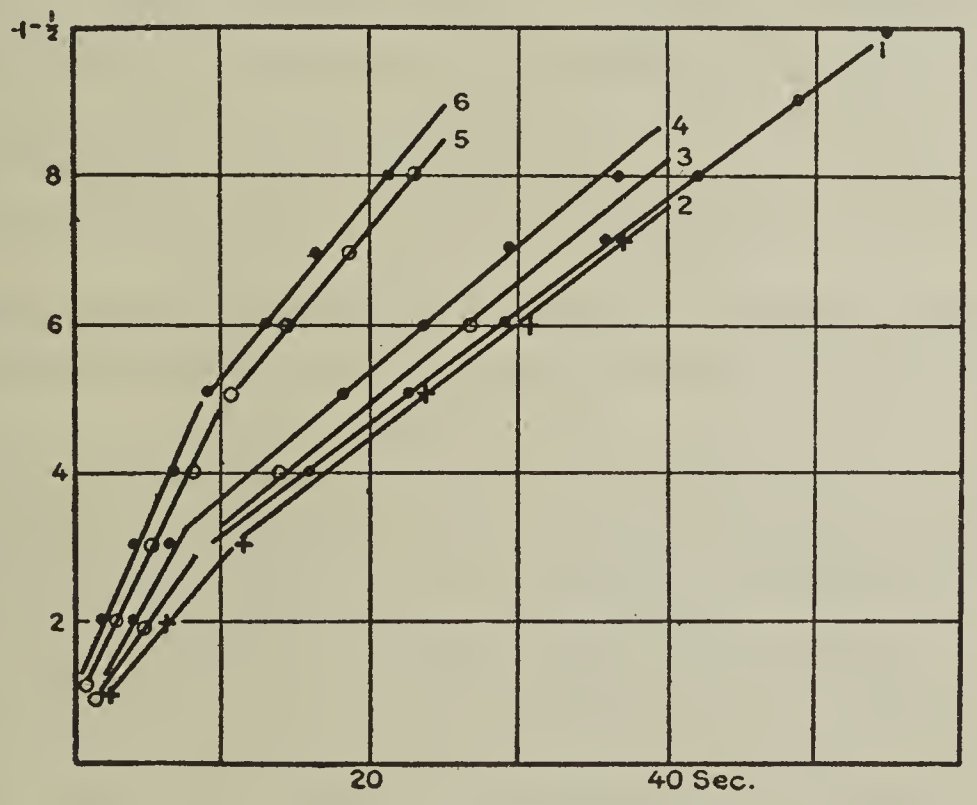


FIG. 89—Specimen 1, fused

Exposures for 1, 2, 3, 4, 5, and 6, were 5, 10, 20, 40, 50, and 60 seconds. Intervals approximately 100 seconds

good conductor of heat, the luminescing material as a whole is probably not at so high a temperature as the surface of the fused specimen. It is possible that this luminescence seen throughout the natural crystal may be the result of secondary radiations such as X-rays or ultra-violet light and that the clear crystals are transparent to it.

Another possibility is that a surface film forms over the fused specimens upon bombardment, diminishing the power of succeeding excitations to penetrate to the phosphorescing centers. This, however, seems improbable, because the fused specimens change very little in appearance under cathode rays and are relatively permanent compared with natural crystals, which, as is well known, discolor very rapidly upon bombardment. Although the period of the fused specimen is shortened by repeated bombardments, it is restored to its longer duration by a time of rest.

The idea also suggests itself that the difference in behavior between the fused and natural specimens may be due to a fundamental difference in the nature of the radiators producing the phosphorescence. In the case of the fused specimens, the phosphorescent light is practically all in the red end of the spectrum, due to the line-like bands which are so conspicuous in this region. In the case of the natural crystals the luminescence comes from broad, diffuse bands. It seems possible that the vibrators producing the very sharp, narrow bands of the fused specimens are atomic. As has been previously suggested, they may be rare-earth atoms which have taken the place of other atoms in the regular crystal lattice of calcium oxide, the limitations imposed by this lattice accounting for the sharp lines in the luminescence spectra. The vibrators producing the banded spectra of the natural fluorites may be molecular in nature. The difference in the effect of the cathode-ray bombardment upon two such different sources of emission may account for the observed differences in the effect of repeated bombardment upon the period of phosphorescence.

IV. THE EFFECT OF X-RAYS ON THERMO-LUMINESCENCE

[Based on experiments of Frances G. Wick and Mabel K. Slattery.]

(A) Fluorites[1]

During the course of the investigations described in sections II and III of this chapter,[2] in which some preliminary experiments were made to test the effect of radiations of various kinds upon the luminescence of fluorite and other materials, exposure to X-rays was found to produce a very marked effect upon thermo-luminescence. Some specimens having no natural thermo-luminescence acquired this property as a result of exposure to X-rays, others did not. Of the naturally thermo-luminescent specimens examined, some were changed little or not at all by the exposure, but many were greatly changed in intensity, in the temperature at which the luminescence appeared, and in the rate of decay. In some cases distinct changes in color resulted. Crystals of fluorite and calcite showed such marked effects that a detailed study of a number of specimens was made.

Specimens of fluorite which were not naturally thermo-luminescent all became so to a greater or less degree upon exposure to X-rays. Crystals which possessed this property naturally had the effect greatly increased and many of them acquired, in addition to the luminescence of the original color, a new and entirely differently colored luminescence which flashed up before the thermo-lumines-

[1] The following account is from the paper of Miss Frances G. Wick, published in the Journal of the Optical Society of America, XIV, 33–44, 1927.

[2] See Frances G. Wick. Phys. Rev. (2), XXIV, p. 272; Wick and Gleason, Jour. Opt. Soc. Am., VI, p. 369, 1924.

cence of the natural crystal appeared when the specimens were heated. Many of the most brilliant specimens had such rapid variations in color as to make quantitative measurements impossible. A number of specimens were found, however, in which the intensity was great enough and the decay comparatively slow and with no rapid color changes, so that photometric observations were possible. A study of the following is included in the present account:

I. The effect of variation in temperature upon the decay of thermo-luminescence in the natural specimens; in the natural specimens after exposure to X-rays; in the same materials exposed to X-rays after heat treatment to take out all natural thermo-luminescence.

II. The effect of time of exposure to X-rays upon the maximum brightness of thermo-luminescence; the rate of decay.

III. Comparison of the effects produced by exposure to X-rays at ordinary and at liquid-air temperatures.

METHOD OF OBSERVATION

Specimens were powdered in a mortar and sifted through a wire gauze of mesh 70 to the inch in order to reduce them to a standard condition, since it is known that the size of the grain has an effect upon the brightness and the rate of decay of thermo-luminescence. The sifted material was heated upon a small circular electric stove, 2½ inches in diameter, to the front of which was attached a copper plate with a platinum-copper thermo-junction inserted in it, from which temperature was read upon a Leeds and Northrup thermo-couple pyrometer. After the copper plate had reached some desired constant temperature, the material to be observed was placed in a layer of uniform thickness of 0.5 mm. upon a thin copper holder and laid upon the stove. Photometric observations of the brightness of thermo-luminescence were made by the method[1] commonly employed in the study of the decay of phosphorescence, since thermo-luminescence is of the same character as phosphorescence, but appears only within certain temperature limits.

The arrangement of apparatus is similar to that already described in section III of this chapter, and depicted in figure 81. A chronograph was used to record time. The specimen was placed on the stove and the comparison lamp was moved so as to match the specimen at its maximum brightness. The time was recorded on the chronograph and was taken as the zero of time. The carriage was moved back to the next stop and allowed to remain until a match was again obtained. The time was recorded and the carriage moved back to the next stop. This procedure was continued until the end of the

[1] Wick and McDowell. Phys. Rev. (2), XI, 421, 1918.

track was reached or the specimen was too dim for observation. Curves were plotted in the usual way, with the reciprocal square root of intensity as a function of time.

Exposure to X-rays—The exposure to X-rays was made as follows: A tungsten target Coolidge tube of the "bedside" variety was mounted so that the X-rays were directed downward through an opening about 5 cm. in diameter in a lead-glass shield placed around the tube. The material to be exposed to X-rays was spread in a thin layer directly under this opening at a uniform distance of about 11 cm. The tube was run on 2 milliamperes and 45 kilovolts.

OBSERVATIONS AND RESULTS

A series of observations was made upon fluorite from Franklin County, New Jersey. The natural specimen had a strong green thermo-luminescence, the duration of which was sufficiently long to make observations of decay possible. After exposure to X-rays, a

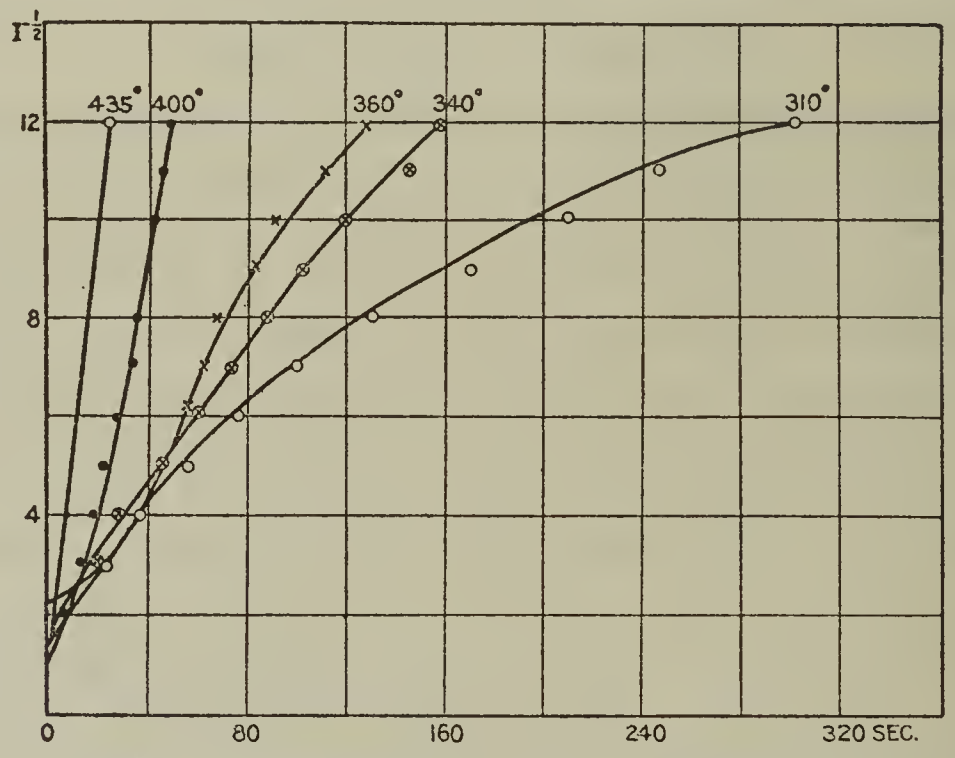


FIG. 90—Natural Franklin fluorite. Decay curves at different temperatures

yellow color appeared which came up before the green did upon heating the specimen and lasted for a very short time. Since cathode-ray spectra show that the fluorites contain as impurities rare earths—a number of different rare earths in each specimen—it seems entirely possible that the yellow color is due to a different impurity from that which causes the green, and that this becomes an activator only after exposure to X-rays. The yellow thermo-luminescence induced by X-rays is not permanent. This yellow flash preceding the more lasting green color appears to be somewhat similar to the effect observed by Karrer and Kabakjian[1] in zinc sulphide activated by radioactive material upon heating. These specimens show a

[1] Karrer and Kabakjian. Jour. Franklin Institute, 186, 317, 1918.

sudden flash, followed by a decrease in brightness, then a second increase in intensity. Specimens of Franklin County fluorite heated until all thermo-luminescence had disappeared and then exposed to X-rays showed, upon being heated, both the yellow flash of short duration and the more persistent green color which came up after the yellow had died out.

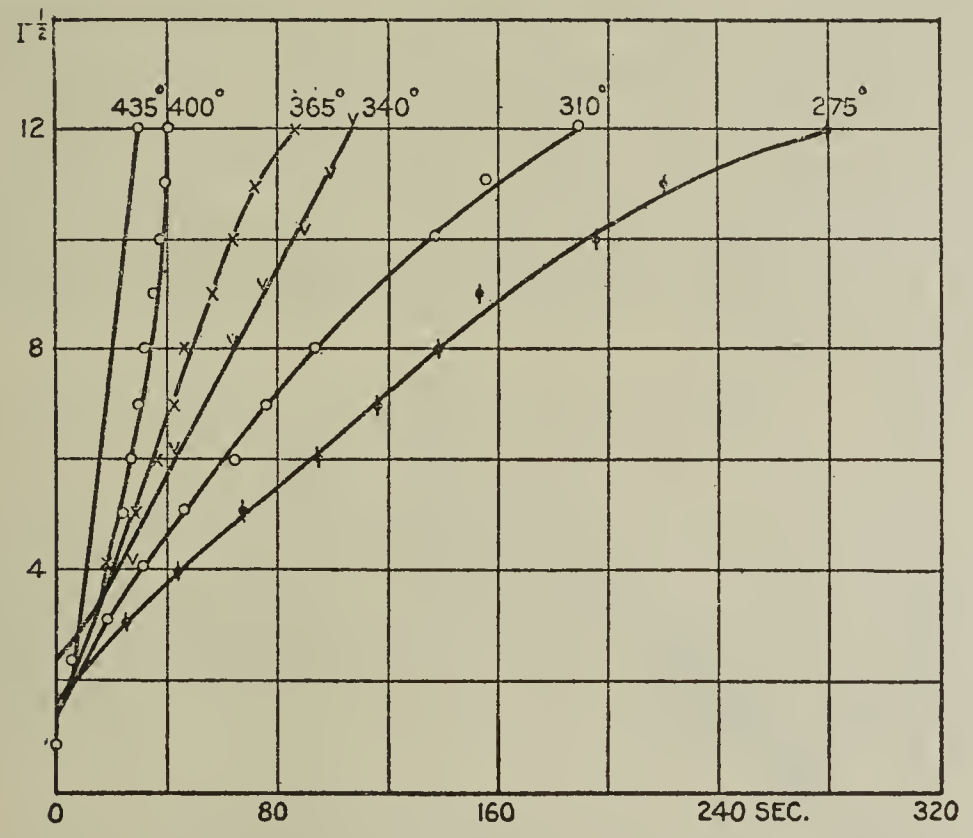


Fig. 91—Heated Franklin fluorite, exposed to X-rays for one hour. Decay curves at different temperatures

Decay curves for the natural material, without exposure to X-rays, are shown in figure 90, the green maximum being taken as the zero of time. Figure 91 shows a corresponding set of curves taken upon material which was heated until all thermo-luminescence had disappeared, then exposed for one hour to X-rays. A comparison of figures 90 and 91 shows that the decay is much more rapid in the heated specimen exposed to X-rays than in the natural one. The curves in figures 90 and 91 resemble those of Ives and Luckeish[1] for the decay of phosphorescence of alkaline-earth sulphides at different temperatures. It is of interest to note that the decay curves at the lower temperatures (figs. 90 and 91) are of the type described by Nichols and Howes[2] as "persistent." As the temperature of observation rises, the curves gradually change to the "vanishing" type.

Observations upon a number of thermo-luminescent fluorites indicate that the effect of exposing the natural material to X-rays is, in general, to increase the brightness and make the decay more rapid. Figure 92 gives a set of decay curves for Franklin fluorite, taken at

[1] Ives and Luckeish. Astro-phys. Jour., XXXVI, p. 330-343, 1912.
[2] Nichols and Howes. Nat. Acad. Sci. Proc., IV, p. 305-312; also section I of this chapter.

a temperature of 310°, which is typical. In curve *A*, for the natural, unexposed material, the decay is slower than that shown in curve *B*, for the natural material after exposure for one hour to X-rays. The decay of the material heated to exhaust all natural thermo-luminescence then exposed to X-rays for one hour as shown in curve *C* is still more rapid.

The effect upon the decay curves at 105° of exposing the natural material to X-rays for different periods of time is given in figure 93; curve *A*, for an exposure of one hour, shows a maximum brightness which is not so great as that for exposure of 10 and 20 hours (curves *B* and *C*) and also a more rapid decay. Increasing the time of exposure from 10 to 20 hours produces comparatively little effect in the thermo-luminescence.

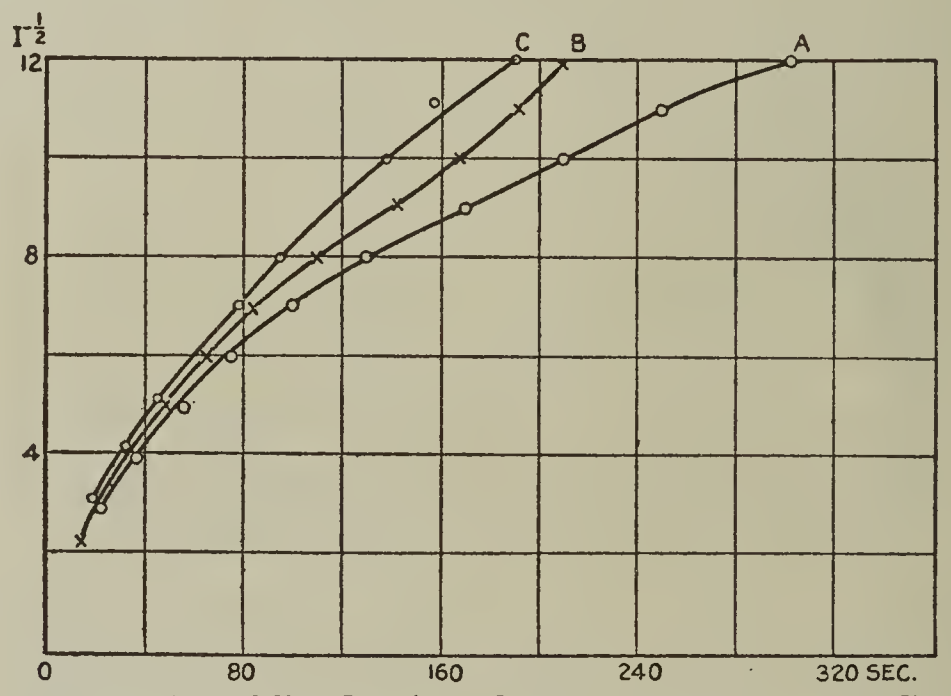


FIG. 92—Franklin fluorite. Decay curves at 310° C. *A*, natural material; *B*, natural material exposed to X-rays one hour; *C*, heated material exposed to X-rays one hour

Figure 94 contains a similar set of curves for the same material taken at the same temperature, heated to eliminate all thermo-luminescence before exposure to X-rays. These curves resemble those of figure 93 in their relation to each other, but it will be observed that the decay is much more rapid than in the case of the unheated material.

Measurements were made upon the length of time required for natural and heated specimens to decay to a definite brightness, that which matched the intensity of the comparison lamp when it was placed at the last stop on the track, at a temperature of 205°, after different lengths of time of exposure to X-rays (fig. 95). It will be observed that, in all cases, the previously heated material takes a shorter time than the natural material and that both curves indicate great irregularity. An increase in time of exposure to X-rays does not always lengthen the time required to decay to the given intensity.

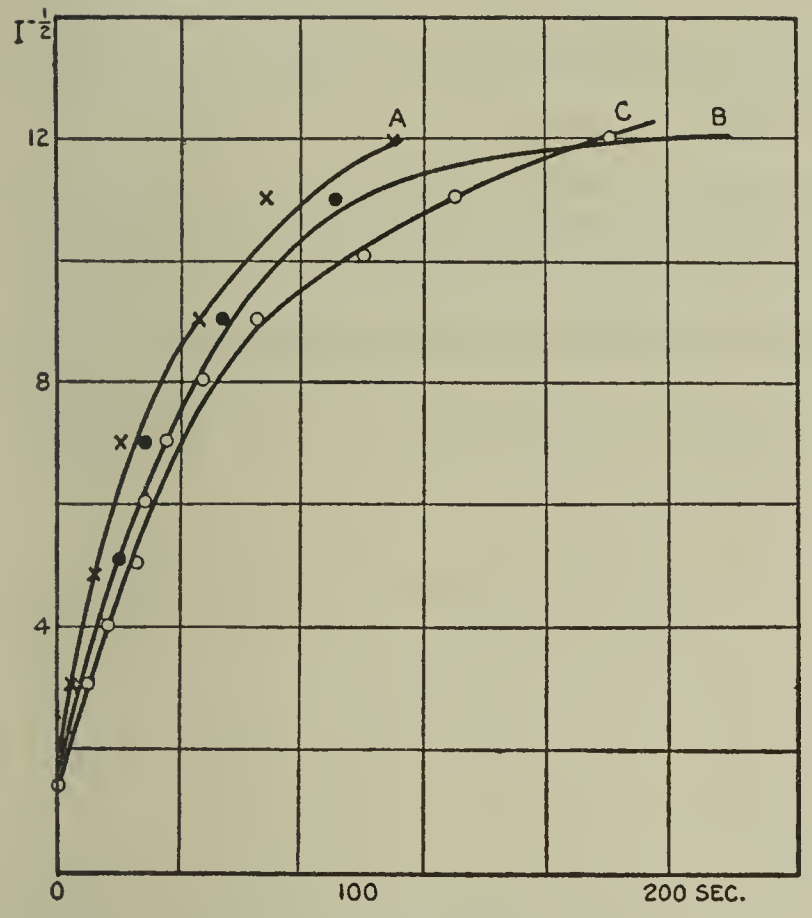


FIG. 93—Natural Franklin fluorite, exposed to X-rays for different lengths of time. Decay curves at 105° C. (Exposures of 1 hour, 10 hours, and 20 hours)

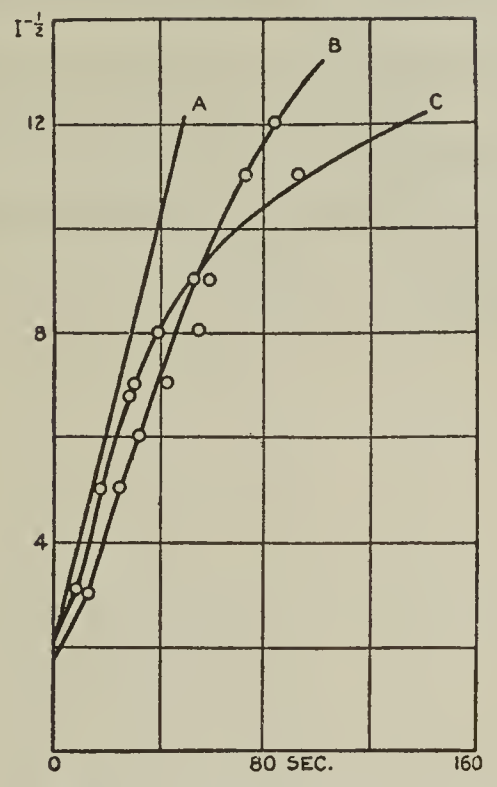


FIG. 94—Heated Franklin fluorite exposed to X-rays for different lengths of time. Decay curves at 105° C. (Exposures of 1 hour, 10 hours, and 20 hours)

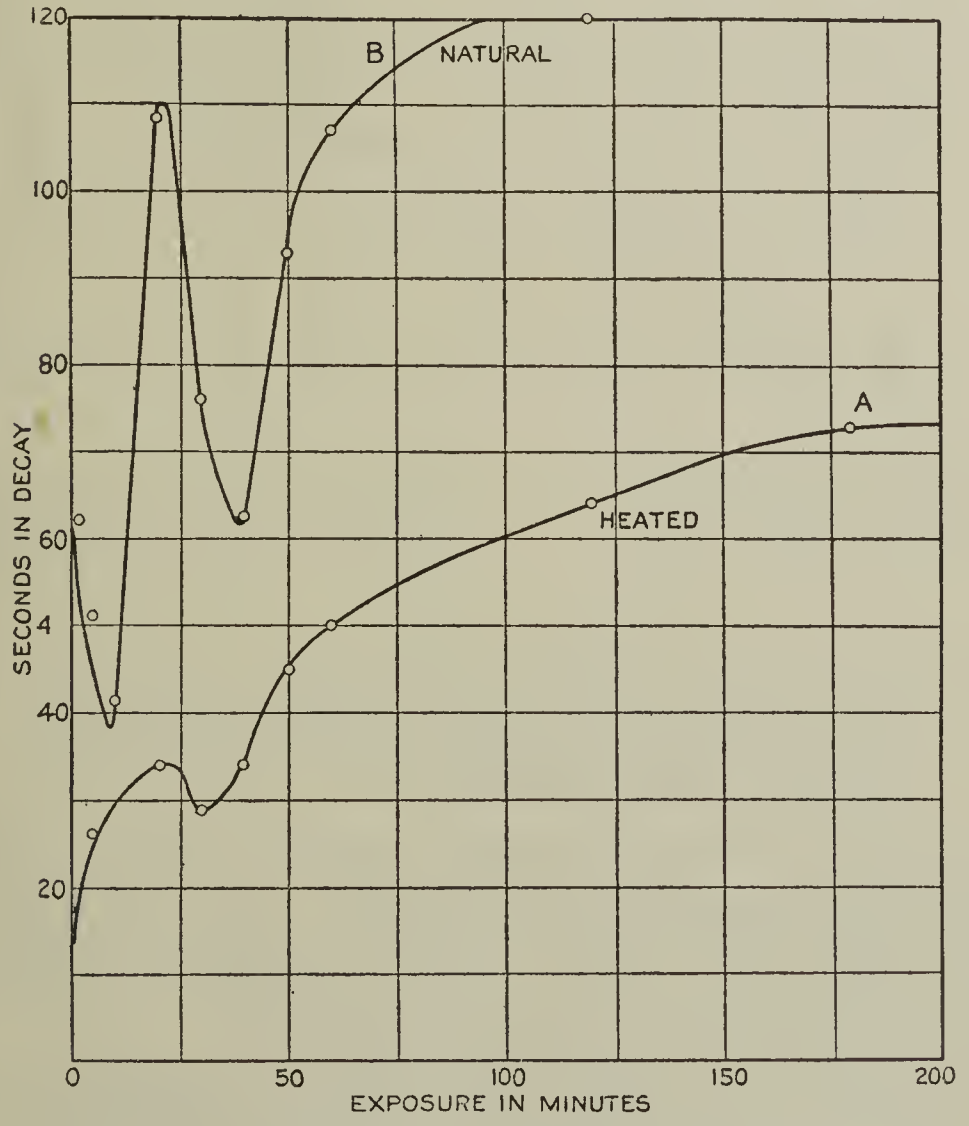


FIG. 95—Franklin fluorite. Length of time required to decay to a definite brightness as a function of time of exposure to X-rays. *A*, heated material; *B*, natural material

There are maxima and minima in both curves for intervals of exposure under one hour. Exposures of more than one hour seem to produce a more regular change in both curves.

The effect of length of exposure to X-rays upon the brightness of the yellow and green maxima of the previously heated material at a temperature of 205° is shown in figure 96. The brightness of the yellow maximum is much greater than that of the green after a given exposure. Increase in the length of time of exposure does not always produce an increase in the maximum brightness of the specimen.

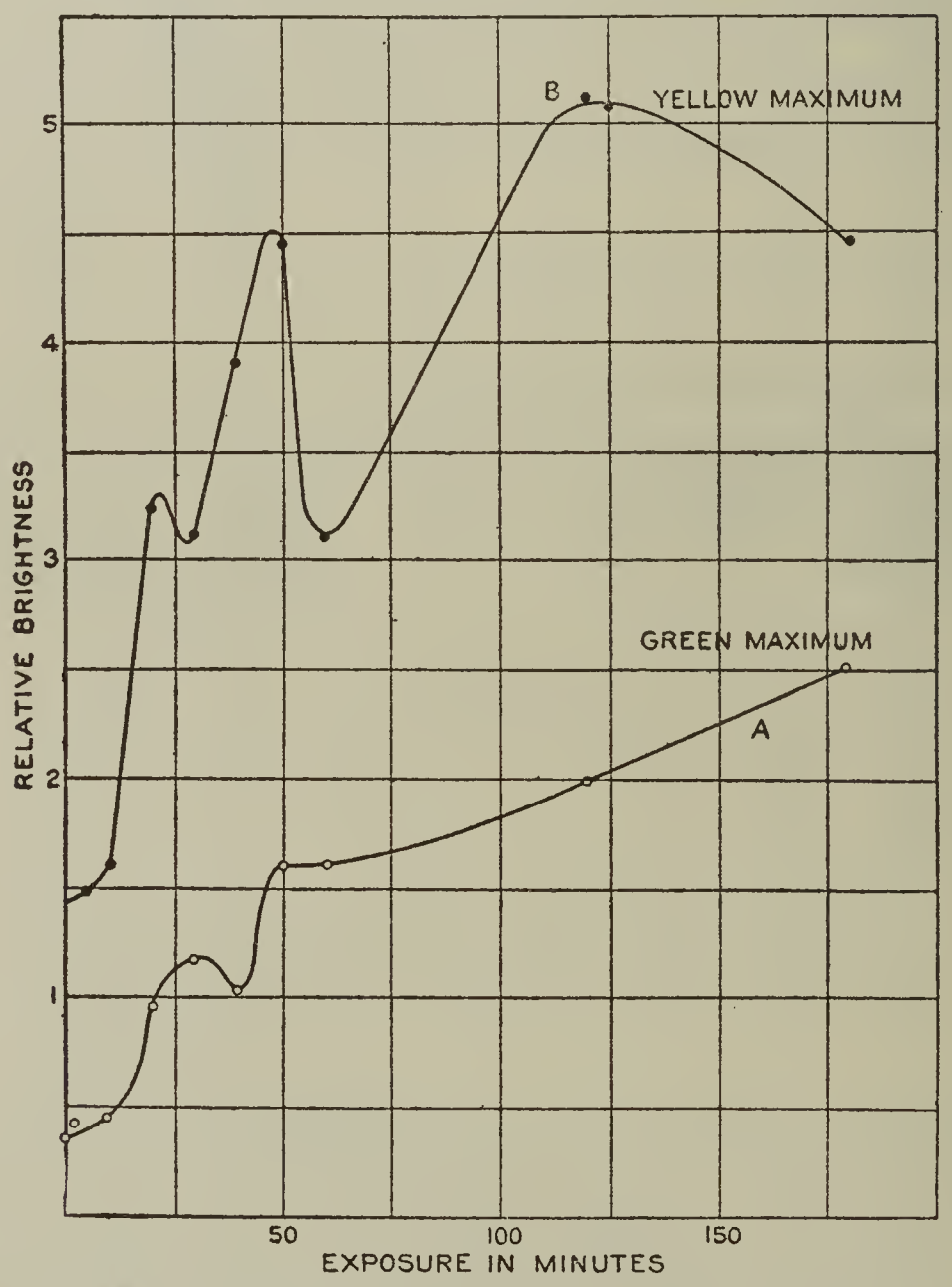


FIG. 96—Heated Franklin fluorite. Brightness of maxima as function of time of exposure to X-rays. Temperature of observation 205° C. *A*, green maximum; *B*, yellow maximum.

The green maximum is more intense after an exposure of 30 minutes than it is after an exposure of 40 minutes. Curve *A*, figure 96, shows a point of inflection at about the same period of exposure as the point of inflection shown in curve *A*, figure 95.

Observations were made upon the relative brightness of the green maximum at different periods of time after exposure of 30 minutes to X-rays. The temperature of observation was 260°. Figure 97 shows that the brightness of the maximum increases during a period

of 50 minutes in which the specimen was allowed to stand in the dark after exposure; then the brightness decreased. This same effect was observed in a number of other samples of fluorite. Measurements were made upon a sample of chlorophane (a thermo-luminescent fluorite) obtained from the late Dr. Charles Baskerville. This material had a natural blue-green thermo-luminescence. Exposure to X-rays introduced a white flash which came up before the green color

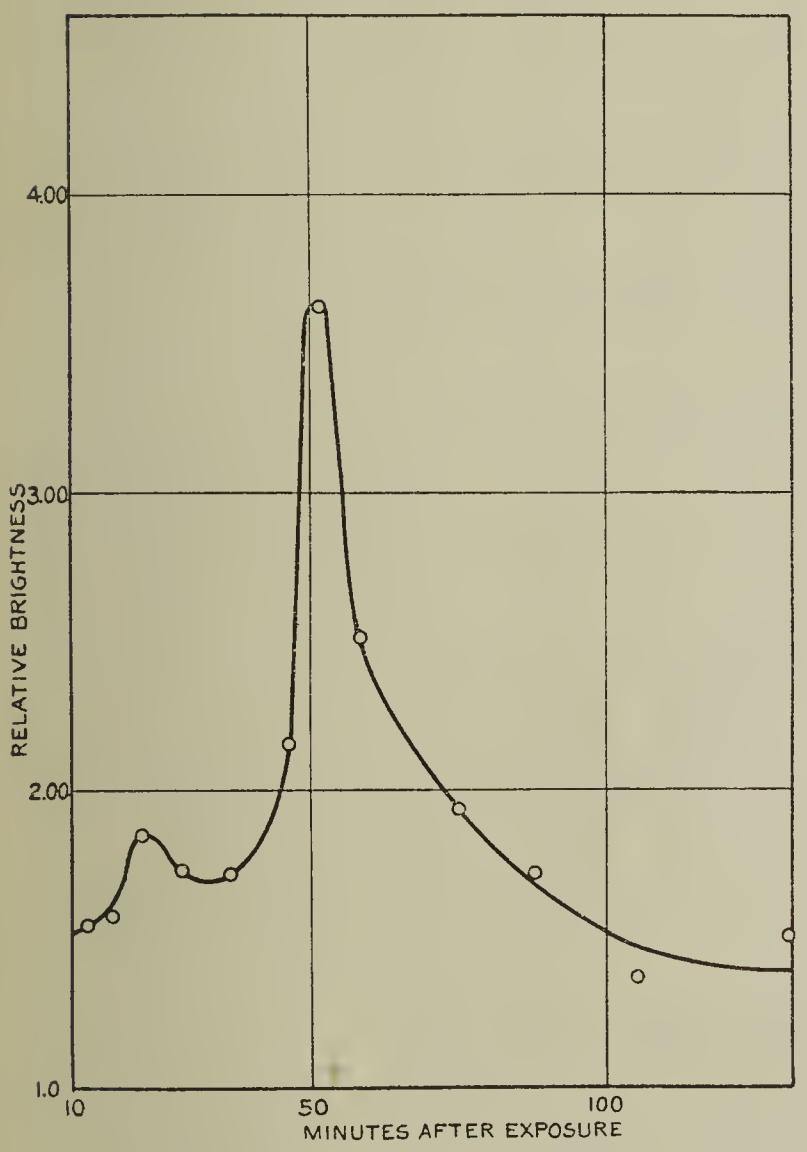


FIG. 97—Natural Franklin fluorite, exposed to X-rays 30 minutes. Temperature of observation 260°. Brightness of green maximum at different lengths of time after exposure to X-rays

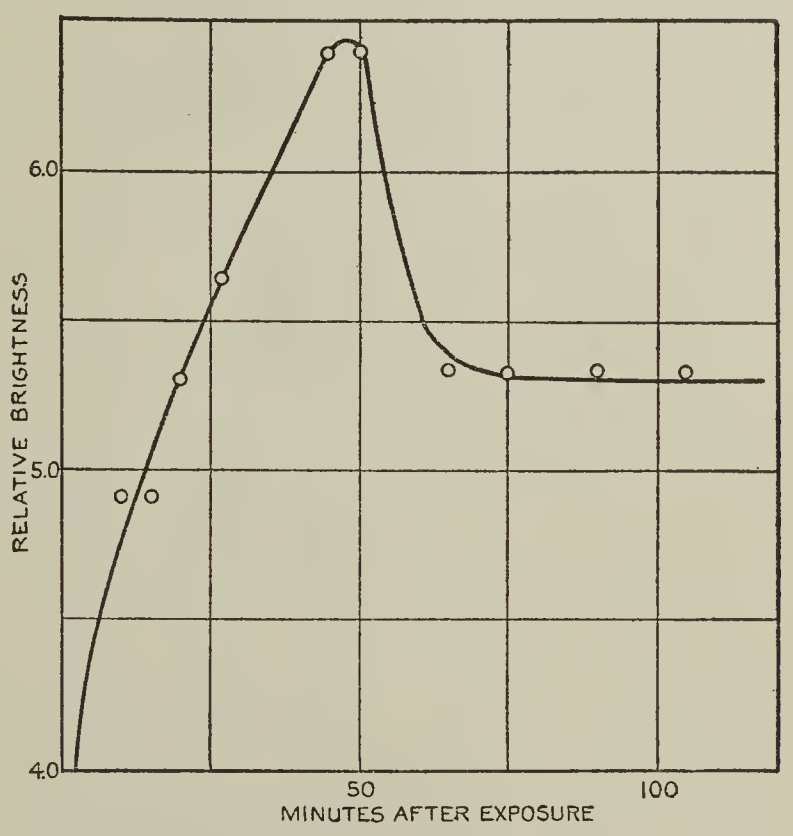


FIG. 98—Chlorophane, exposed to X-rays 75 minutes. Temperature of observation 420° C. Brightness of white maximum at different lengths of time after exposure to X-rays

when the specimen was heated. Figure 98 shows the effect upon the brightness of this white flash of allowing a specimen previously heated to remove natural thermo-luminescence, to stand after exposure to X-rays. The temperature of observation was 420° and the length of time of exposure to X-rays 75 minutes. A distinct maximum is reached 50 minutes after exposure. A specimen of fluorite from Westmoreland, New Hampshire, which had a green flash introduced by exposure to X-rays, was found to have very irregular variations in maximum brightness of this flash within the first hour after exposure to X-rays. (See fig. 99.) This specimen was one of the most

interesting of the fluorites, but the changes in color of thermo-luminescence upon heating made the measurement of decay curves impossible. The natural thermo-luminescence was brilliant purple, consisting of four distinct bands which could be observed through a small direct-vision spectroscope. The approximate limits of the bands were: (1) 0.5750-0.6250μ; (2) 0.5200-0.5350μ; (3) 0.4750-

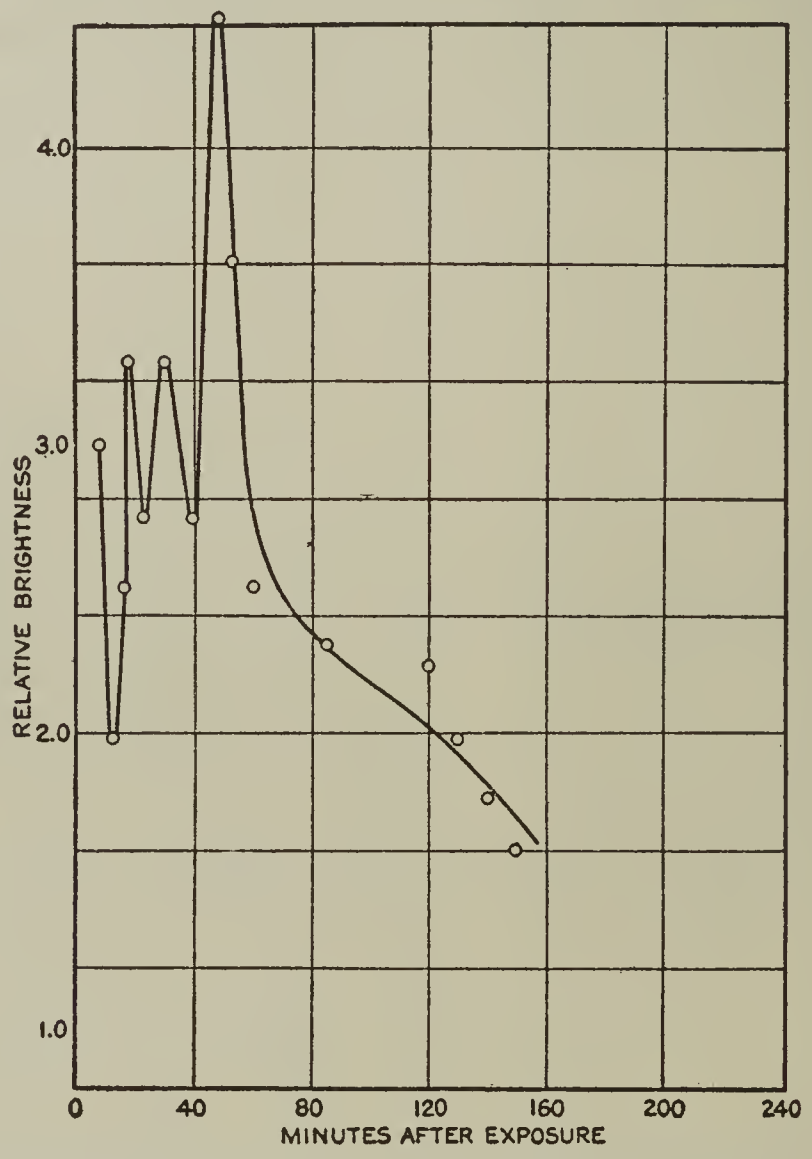


FIG. 99—Fluorite from Westmoreland, New Hampshire, exposed to X-rays 1 hour. Temperature of exposure 263° C.

0.4950μ; (4) a faint band barely visible in shorter wave-lengths. The green thermo-luminescence which resulted from bombardment with X-rays consisted of two distinct line-like maxima at wave-lengths of 5,568 and 5,390. This same green color is observed under cathode-ray excitation, and it is due to terbium. The specimen evidently has a number of different impurities, which may account for the very irregular variation in intensity of the green maximum after exposure to X-rays. Material exposed to X-rays was examined 8 months later and found still to retain the green luminescence imposed by X-rays.

(B) Calcites

Observations were made of three different varieties of calcite kindly furnished by W. P. Headden, of the Colorado Agricultural College, Fort Collins, Colorado. Calcite from an old Crookes tube was also

examined. Exposure to X-rays increased the thermo-luminescence of all the calcites observed. The color of this luminescence was orange. The calcite from Ingleside was given a green luminescence preceding the orange by exposure to X-rays.

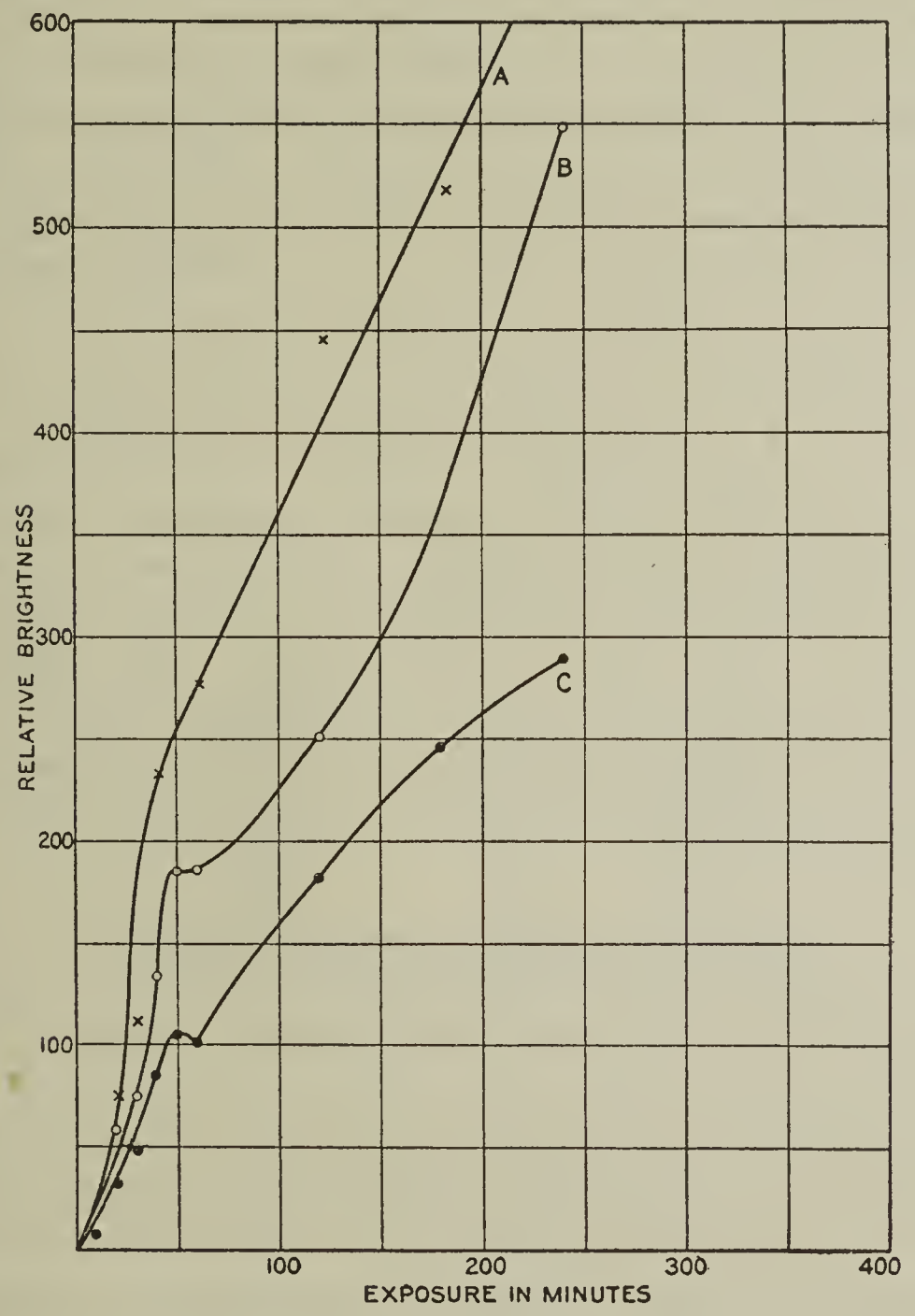


FIG. 100—Fort Collins calcite. Brightness of maxima as function of time of exposure to X-rays. Temperature of observation 275° C. *A*, first flash immediately after exposure; *B*, second flash immediately after exposure; *C*, second flash 50 hours after exposure

Calcite from Fort Collins was most interesting. It had a natural orange thermo-luminescence. After exposure to X-rays an additional luminescence was observed. When the specimen was heated the specimen had a thermo-luminescence which came up as two distinct flashes. The first flash was observed to be a band with limits about 0.5780μ to 0.6800μ. After this had died down a second thermo-luminescence appeared, the limits of which were about 0.5250μ to 0.6500μ. The brightness of the maxima of the first and second flashes immediately after exposure as a function of the time of exposure to X-rays was likewise determined (curves *B* and *C*, fig. 100. Curve *A* shows the second flash 50 hours after exposure. The

first flash had disappeared by this time. These curves show breaks after an exposure of about 50 minutes.

The irregularities occurring in the curves for fluorite and calcite suggest a mechanism which is very complicated. In order to explain the fact that intensity of maximum luminescence is greater after the specimens have been allowed to stand than immediately after exposure to X-rays, Mr. Wilber suggested the following as being in line with the theory of Lenard and Saeland:[1] Under the influence of X-rays electrons are separated from the atoms of metallic impurities in the crystals and these are held in the insulating medium of the phosphor. After the exposure to X-rays is over, the force of attraction between these electrons and the metal atoms brings them nearer the atoms than they were immediately after the exposure to X-rays, so that when heat is applied after a period of time has elapsed since the exposure, there are more combinations producing light than there could be immediately after exposure. It also seems possible that some change is started under the influence of X-rays which does not stop immediately after exposure has ceased. The possibility of a very slow radioactivity might also be suggested, since the flash in many of the materials examined resembles that described by Karrer and Kabakjian as taking place in zinc sulphide activated by a radioactive compound.

(C) Some Synthetically Prepared Materials

The work included here was undertaken as a sequel to the study of the effects of X-rays on thermo-luminescent calcites and fluorites just described.

The effect of X-rays in restoring activity to thermo-luminescent minerals[2] which have been de-activated by heating is well known.[3] In general, it is assumed that this ability to fluoresce at high temperatures is due to the presence of traces of impurities, the spectral nature of the light obtained being dependent upon the impurity involved. In some cases it is possible by a study of the light emitted to identify the impurity present.

Identification of the impurity, however, is not a simple matter. Sometimes several activators are present in a given crystal, the resulting spectrum being very complex. The amount of impurity is too small to be detected by ordinary chemical analysis; as a result, a quantitative estimate is impossible.

It seemed advisable, in view of the uncertain composition of the natural materials, to make some thermo-phosphors of known com-

[1] Lenard and Saeland. Ann. Physik, 28, p. 476-502, 1909.

[2] Activation of the natural crystal possibly was due to radioactive transformations or even exposure to the new cosmic ray over very long periods.

[3] Bayley, Phys. Rev. (2), XXIV, p. 495; Wick, Phys. Rev. (2), XXIV, p. 272; Wick and Gleason, Jour. Opt. Soc. Am., 6, p. 369, 1924.

position. From these it might be easier to deduce the quantitative effects due to exposure to X-rays.

Several synthetically prepared substances which showed luminescence in a cathode-ray tube were examined for thermo-luminescence. They showed no effect upon heating before exposure to rays. After exposure to X-rays, varying from one to two hours, from a tube run at 2 ma. and about 45 kv., these same samples showed a luminescence when heated. The color of the thermo-luminescence usually corresponded to that observed in the cathode-ray tube. Table LI gives a list of the observations.

TABLE LI—*Thermo-luminescence after X-ray exposure.*

Material	Thermo-luminescence (at approx. 250° C.)	
	Unexposed	Exposed ½ hour
Tested pure $CaCO_3$.....	None	None
Tested pure CaO.....	None	None
CaO+erbium.....	None	Violet and blue
CaO+samarium.....	None	Orange
CaO+dysprosium.....	None	Yellowish white
CaO+neodymium.....	None	Faint blue
Tested pure $CaSO_4$.....	None	None
$CaSO_4$+manganese.....	None	Bright green

Of these substances, $CaSO_4 + Mn$ seemed the most desirable for further study, since it gave a high color which could easily be matched by combining color-screens. These samples would not easily be affected by exposure to the moisture of the air, as were the samples of CaO.

Two samples were made, one containing twice as much manganese as the other. The method of preparation was to evaporate to dryness a mixture of $CaSO_4$ with $MnCl_2$, and NH_4OH. This was sifted through 70-mesh and then heated to a bright-red heat for about an hour in a quartz crucible with a blow torch. The porous mass resulting was pulverized and again passed through 70-mesh to insure uniformity of size and homogeneity of material. It was found from previous experiments with natural thermo-luminescent materials that the size of the grain affected the luminescence. Sample A contained 25 c. c. 0.01 molar solution of $MnCl_2 : 4\ H_2O$ for 20 grams of $CaSO_4$. Sample B contained 50 c. c. of the same solution for 20 grams. Calculation shows sample A to contain 1 atom of manganese to about 500 molecules of the solvent $CaSO_4$; sample B has about 250 molecules of solvent to each atom of activator: sample A, 1 : 465; sample B,

1 : 230. A glance at figure 102 will show that the concentration for optimum brightness is probably nearer the higher concentration.

Spectroscopically, the luminescence obtained on heating was a green band extending from 0.4800μ to 0.5600μ. At comparatively low

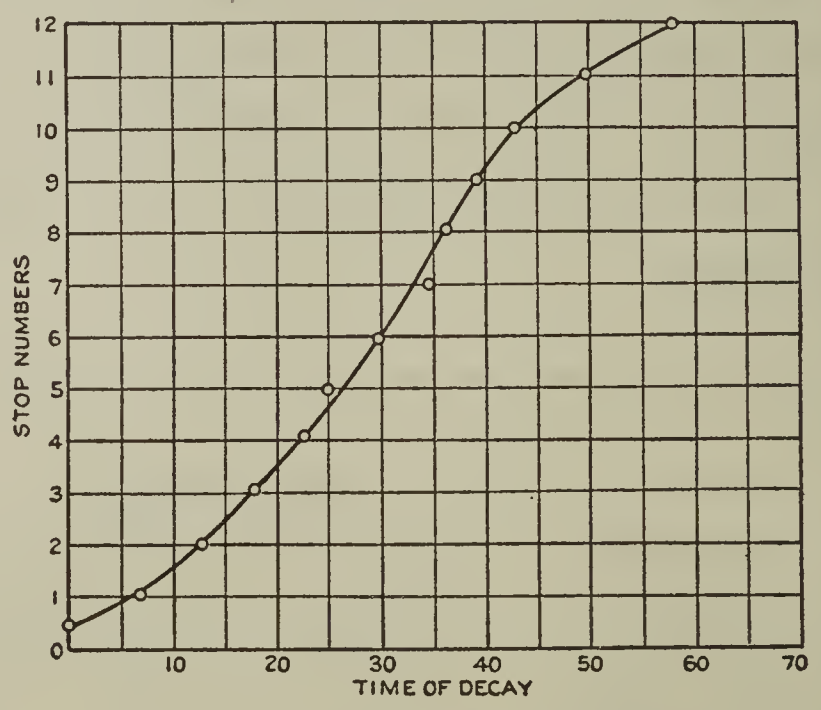


Fig. 101—Curve of thermo-luminescence decay, Mn in $CaSO_4$. 1 : 250. Temperature 120° C.

temperatures (200° to 300° C.) the decay of luminescence was very rapid, but at 120° the fading was slow enough to make a determination of curves of decay possible. The method of observation described in the opening paragraphs of this part of Chapter VII were used.

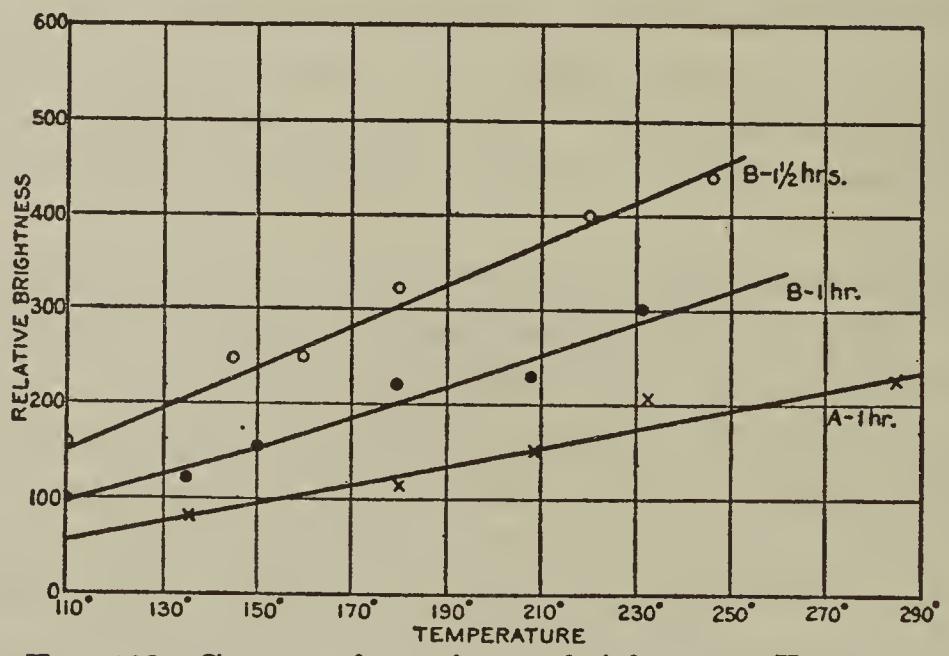


Fig. 102—Curves of maximum brightness. Temperature varied. Mn in $CaSo_4$. *A*, 1 : 500; *B*, 1 : 250

Measurements were made on sample B (1 : 250) exposed for one hour to the X-rays. Figure 101 shows the decay to be of the persistent type.

The effect of temperature to which the substance was treated, after exposure to X-rays, upon the brightness of the maximum was

observed. Figure 102 shows the results. In general, the curve approximates a straight line for both samples. Increasing the length

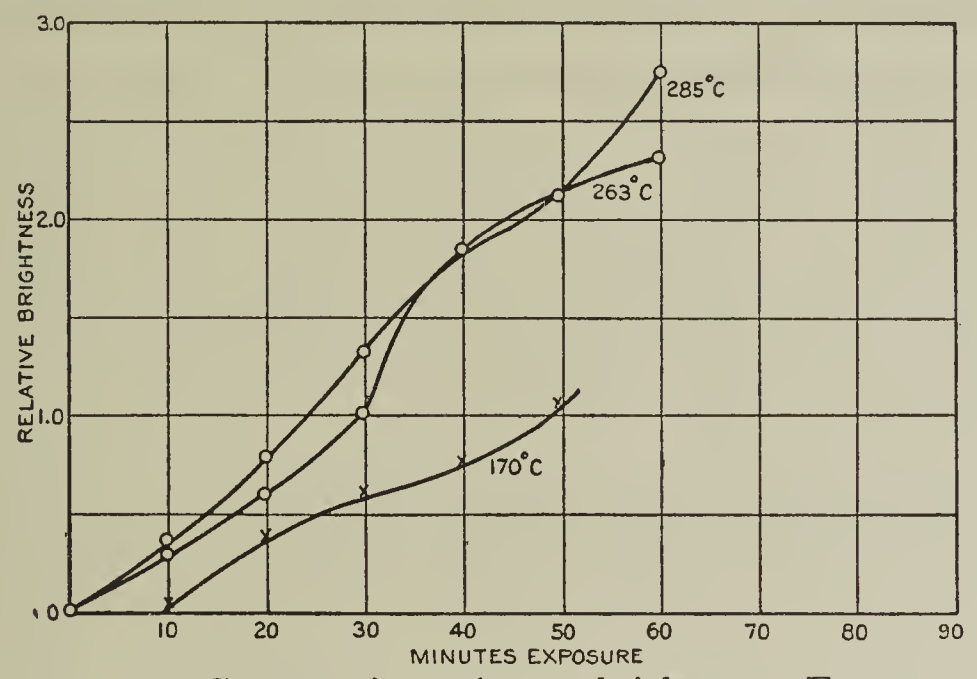


FIG. 103—Curves of maximum brightness. Exposure varied. Mn in $CaSO_4$. 1 : 250

of exposure increases the brightness of the maximum at a given temperature, as can be seen by comparing the two curves for B.

To examine the effects of varied lengths of exposure on the maximum brightness, observations were made at different temperatures on both samples. For the sample containing the smaller amount of manganese at the temperatures 170° and 263° C. the brightness is seen to increase gradually with the length of exposure, but a satura-

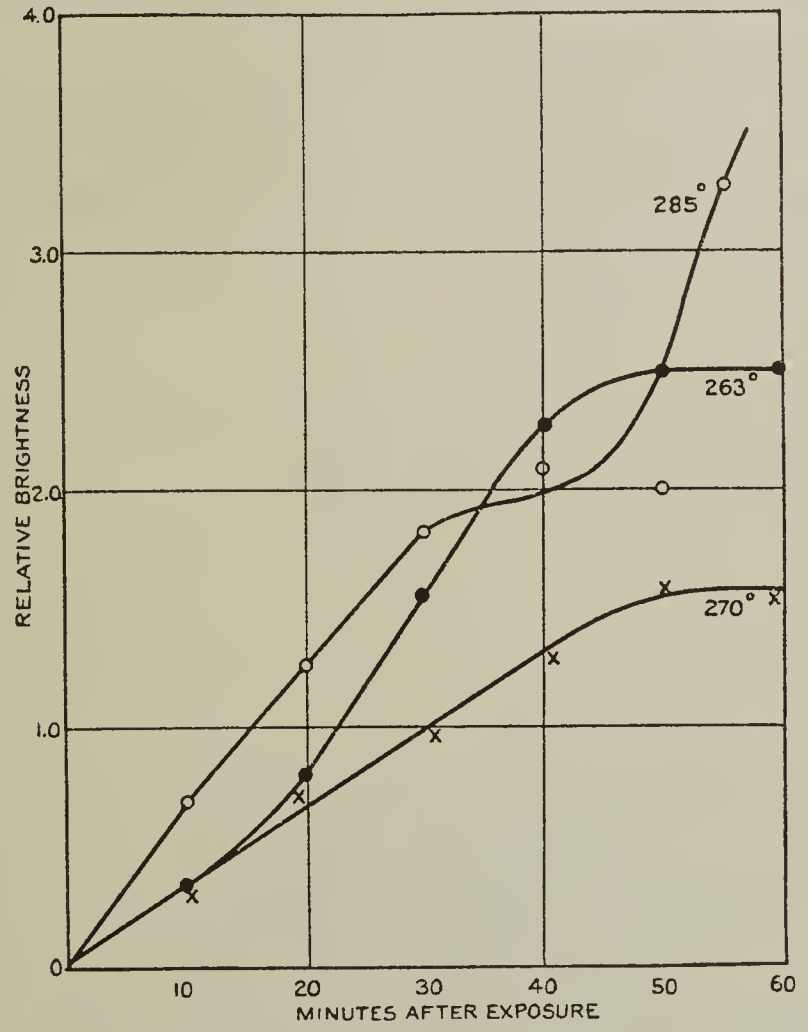


FIG. 104—Curves of maximum brightness. Exposure varied. Mn in $CaSO_4$. 1 : 500

tion is reached in about 50 minutes. At a higher temperature (285° C.) no maximum is reached within the hour for either sample. Figure 104 is for sample A (1 : 500). Figure 103, for sample B (1 : 250),

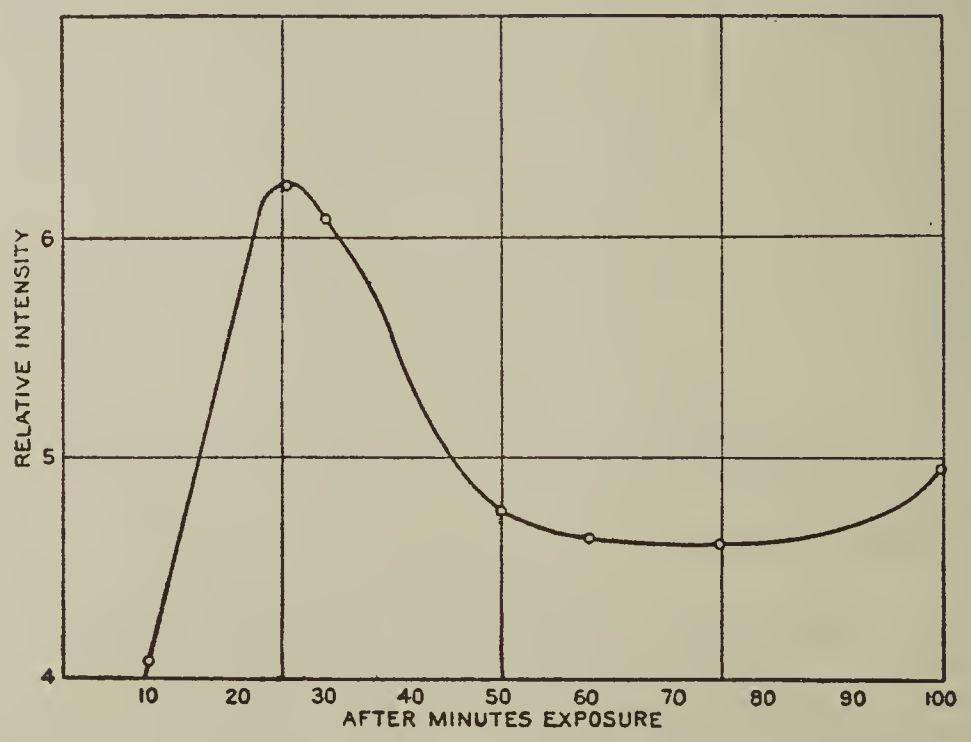


FIG. 105—Curve of maximum brightness. Time after exposure varied. Mn in $CaSO_4$. 1 : 250

shows that a longer exposure would be required to reach a saturation, due to the increased amount of activator.

With the fluorites and calcites it had been observed that the activity imparted to the materials by X-rays was not permanently fixed, but

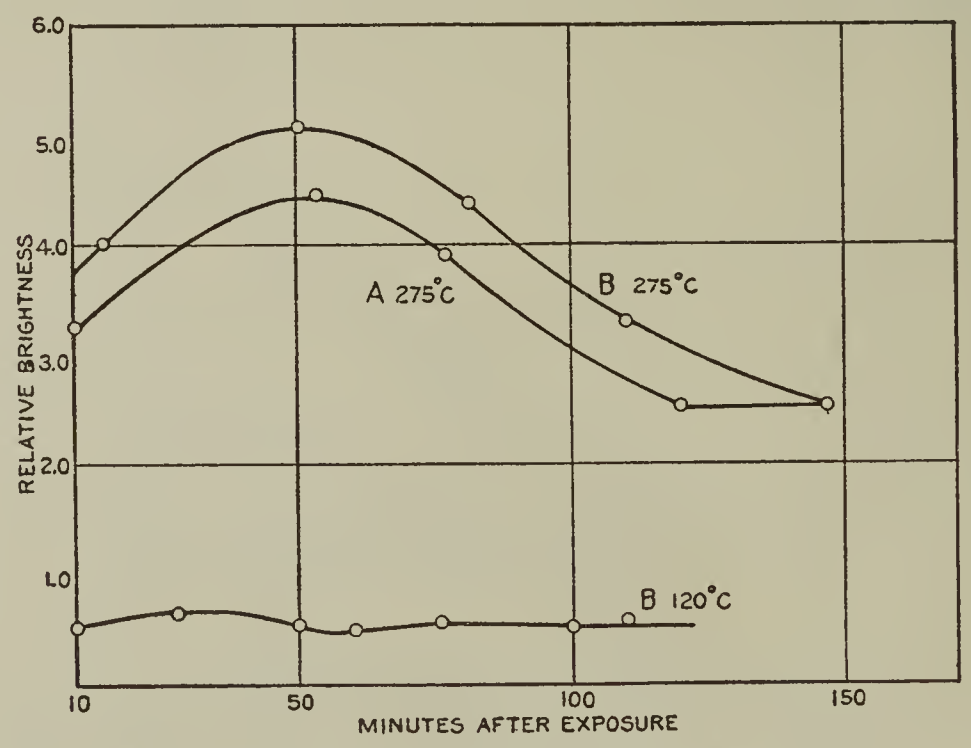


FIG. 106—Curves of maximum brightness. Time after exposure varied. Mn in $CaSO_4$

decayed slowly on standing, like the effect of slow phosphorescence. This study showed also an apparent increase in activity about half an hour after exposure to the rays. To examine the effect of decay with time we made a series of measurements of the brightness of the maximum for a specimen rayed for a certain length of time and

heated always to the same temperature, allowing about 10 minutes between each reading.

Figure 105 shows the results obtained from sample B (1 : 250) exposed to the rays for one hour and heated to a temperature of 120° C. There is a brighter maximum 27 minutes after the exposure than immediately after the raying was stopped. Figure 106 shows the same effect at a higher temperature for both of the samples. The maximum here appears at about 50 minutes after exposure. The lowest curve is from figure 105 plotted to the same scale.

The same experiment was made with CaO containing a small amount of samarium. The sample was rayed for 65 minutes, and the brightness of its yellow maximum at a temperature above 420° was examined as a function of the length of time after exposure. This, too, shows a maximum (fig. 107) at about 30 minutes after the

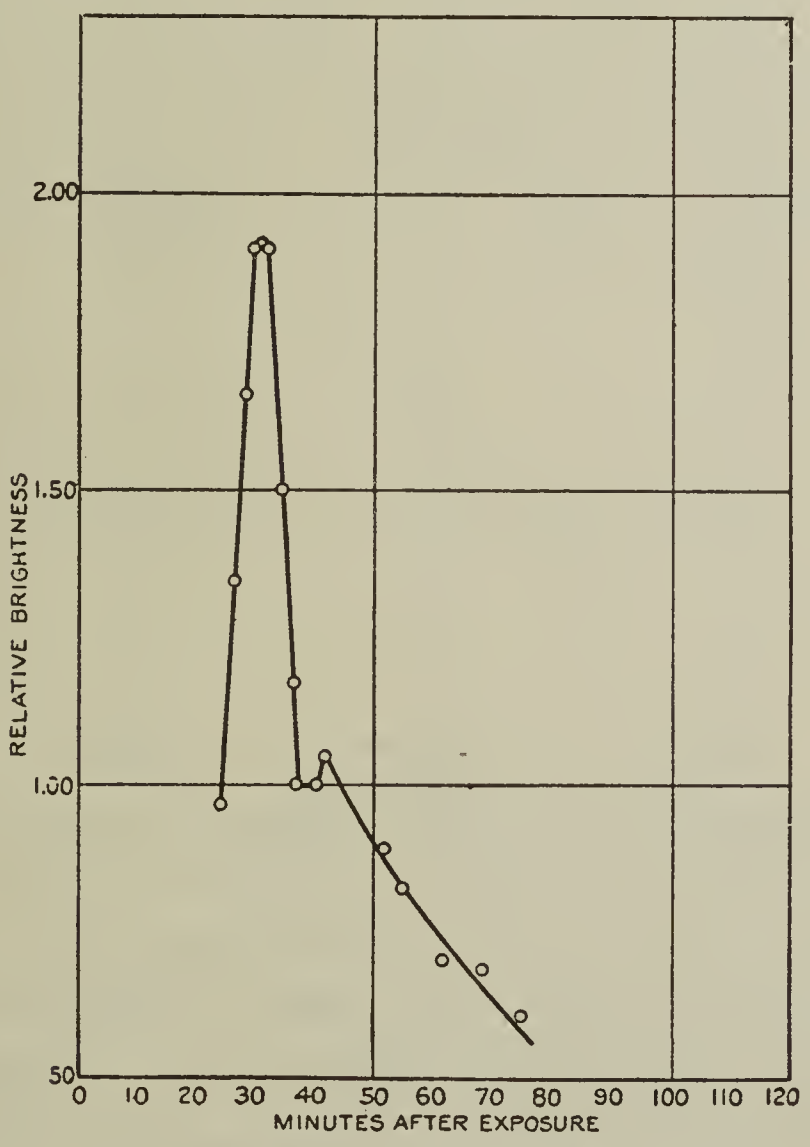


FIG. 107—Curve of maximum brightness. Minutes after exposure varied. Samarium in CaO

exposure ends. The steepness of the curve is probably due to the high temperature to which the substance was heated.

It would seem that this increase in activity is a characteristic of all thermo-luminescent materials, independent of the nature of the solvent or activator. It has been found in every one so far tested—

calcites, fluorites, chlorophane, Mn in $CaSO_4$, and Sm in CaO. A somewhat similar effect has been observed in photography.[1]

Figure 108 deals with the effect of lowering the temperature at which the specimens were exposed. All previous measurements were made at room temperature. A portion of sample B was placed upon a thin copper block, which was used as a lid for an evaporating-dish, filled with a mixture of ice and $CaCl_2$. The sample was then rayed for 30 minutes. No attempt was made to measure the exact tem-

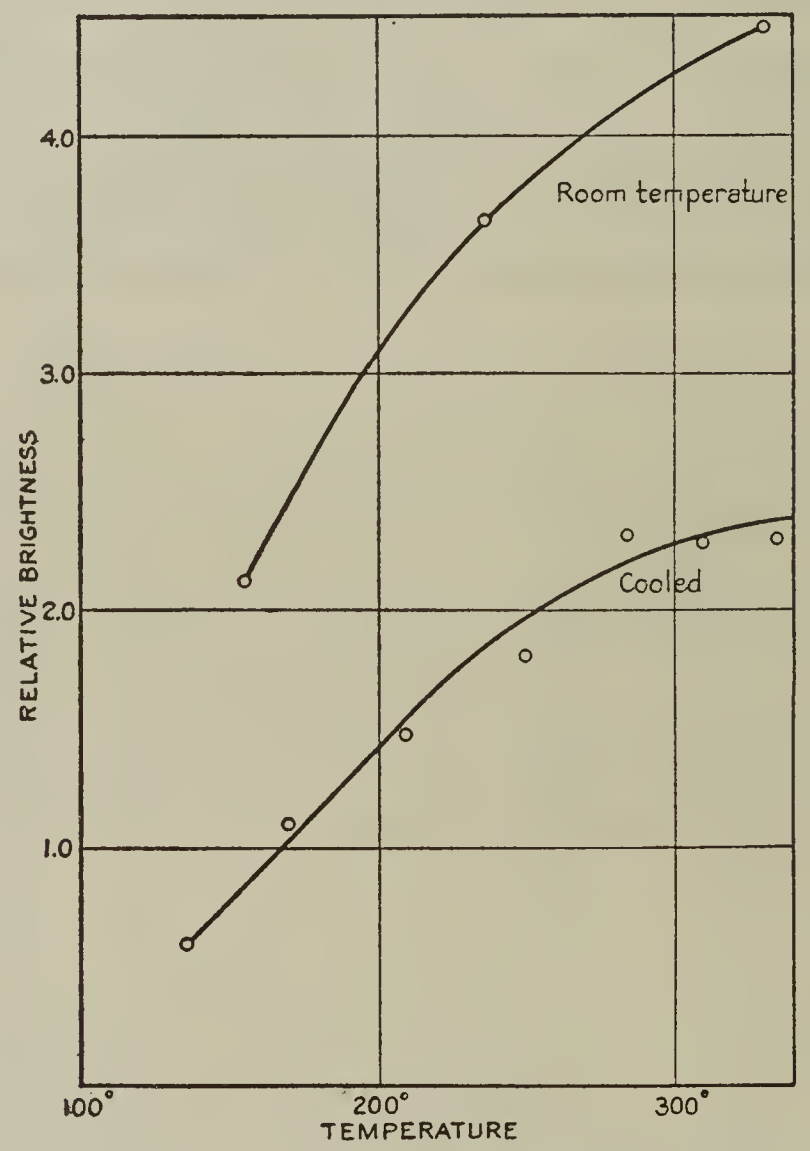


FIG. 108—Curves of maximum brightness. Temperature of exposure and temperature of observation varied

perature. At the end of 1 hour and 40 minutes, when the maximum effect of time should be past, the effect of temperature upon the brightness of the maximum was determined. Another portion of the same specimen was rayed on the same copper block, in the same position, for 30 minutes, at room temperature, and allowed to rest

[1] C. F. Brush presented a paper at a meeting of the American Philosophical Society some time ago on the effect of variation of time between exposure and development on the intensity of the photographic image. It was shown that for some plates there was an increase in blackening if the plate was left for a few minutes after exposure. The experiment was repeated here by Professor G. S. Moler with time intervals varying from a fraction of a second to 19 minutes. For the plate used (ordinary Seed 26), a distinct increase in intensity was found when development began 8 minutes after exposure. This could not be duplicated with all plates. It is not surprising to find the same effect in both cases, since both are examples of a change due to radiation.

for 100 minutes, the same as the previous sample. The effect of temperature on the brightness of maximum is shown in figure 108. The specimen evidently stored a greater amount of energy than at a lower temperature.

SUMMARY

(1) Traces of manganese in solid solution in $CaSO_4$ make the substance susceptible to the action of X-rays.

(2) The thermo-luminescence is green in color (0.4800 to 0.5600μ).

(3) The luminescent decay at 120° shows a curve of the persistent type (fig. 105).

(4) The maximum brightness for a given substance after exposure shows a straight-line relation with temperature (fig. 102).

(5) Saturation is reached for low temperatures (260°) within an hour exposure to the rays (figs. 103 and 104).

(6) Synthetic thermo-phosphors show an increase in activity on standing a few minutes after exposure (figs 105 to 107).

(7) Decreasing slightly the temperature at which a specimen of Mn in $CaSO_4$ was exposed caused an apparent decrease in energy stored.

PART II

CANDO-LUMINESCENCE

(THE LUMINESCENCE OF INCANDESCENT SOLIDS)

With text-figures 109–169

CHAPTER VIII

THE FLAME EXCITATION OF LUMINESCENCE[1]

I. PRELIMINARY OBSERVATIONS

The existence of a definite, well-defined upper limit of temperature above which bodies are neither phosphorescent nor fluorescent has long been accepted in the science of luminescence. Lenard and Klatt,[2] as was stated in a previous chapter, estimated roughly the temperatures of extinction of the after-glow and of fluorescence for the phosphorescent sulphides. The "upper momentary-range" in their scheme of temperature relations lies between the extinction temperature of phosphorescence and the still higher temperature at which fluorescence ceases.

The precise boundaries of this region were left undetermined, but their tables show fluorescence to be in general very dim or entirely gone at 400°. In the case of Ca-Bi, Sr-Cu, Sr-Zn, and Sr-Bi they were still able to detect traces of it when the substance was at a dull red heat. Phosphorescence usually disappears at a much lower temperature (200° to 300°). There are, however, instances of visible radiation at somewhat higher temperatures which are suggestive of luminescence, and the study of one of these, in particular, was the starting-point of the present investigation.

When the oxygen of an oxy-hydrogen blast-lamp used in the production of the lime-light is turned off and the hydrogen flame is allowed to play over the surface of the slowly cooling lime cylinder, a greenish light may sometimes be seen in the regions reached by the flame. This furtive glow, which occurs at temperatures corresponding to a very low red heat, or below, must have been familiar to many of the early users of the projection lantern.

Herbert Jackson, in a lecture in 1898 on phosphorescence, alludes to "the fact that many substances will phosphoresce *during and after exposure to the flame of hydrogen.*" He says further in substance:

"The flame of coal gas burnt in a Bunsen burner will excite phosphorescence in many specimens of lime; but the effect is not strong enough to be shown to an audience . . . If such a body as lime could be obtained in a very porous condition, it might, *while acting as an inducer of chemical combination, itself respond to oscillations arising out of that combination.*

"This is found to be the case. *A jet of unlighted coal-gas* allowed to play over *warm porous lime produces a slight phosphorescence,* very faint but quiet visible in a dark room. By dusting easily volatile substances such as finely powdered resin over *slightly heated lime,* the oxidizable vapor is brought more

[1] Nichols and Wilber. Phys. Rev. (2), XVII, 453, 1921.
[2] Lenard and Klatt. Annalen der Physik, XV, p. 425, 1904.

closely into contact with the lime, and the phenomenon of phosphorescence is made more visible . . .

"Lime which showed a *green glow* in the vacuum tube gives a *green glow* with the powdered resin. So also in the case of the *orange* and *blue* yielding limes. The possibility of the phosphorescence being due to the resinous vapor was excluded by control experiments. This phosphorescence was often well seen when some of the limes were being prepared in a furnace.

"Many substances retain the power of phosphorescing at a high temperature especially if they are in a very fine state of division or not quite pure. Most of the limes were made from *organic salts of calcium*, and as the organic matter burnt away, a thin and scarcely visible flame played over the top of the crucible in which the calcination was carried out. It was frequently quite possible to predict by watching the *glow* which was developed in the lime, what color would be given when the phosphorescence was brought about by such sources as the jar-spark or the discharge in vacuo."

Attempts to produce this effect in somewhat modified form led the present writers to a number of striking results. In the first experiments air-slaked lime from old lime-light cylinders which had broken down under exposure to the atmosphere was inserted in a hydrogen flame.

For convenience, the powder was placed on a fine wire gauze and rubbed into the mesh. It was immediately noted that when the flame was applied from above, a yellowish green glow occurred in those parts of the surface of the oxide which were within certain zones of the flame.

When the flame was applied underneath the gauze, heating it to about the same temperature, no glow appeared on the upper surface, but only on such portions of the oxide as protruded through the mesh and were *directly bathed by the flame.* When the hydrogen jet was below but the gas was ignited only above the gauze, the glow appeared in a ring-shaped zone at the outer base of the flame. When the flame struck through the gauze or was purposely ignited below the gauze, the glow almost or entirely disappeared on both the upper and lower sides of the gauze.

By repeating these observations, with such modifications of material and method as suggested themselves, we were soon able to establish the following facts:

(1) *The effect is not an ordinary temperature radiation;* it exists only in a comparatively narrow range of temperature within which it rises, reaches a maximum, and disappears.

(2) It sometimes greatly exceeds in intensity the black-body radiation for the same temperature.

(3) It is not producible by heating to the required temperature either electrically, as on a heated strip of metal, nor by radiation or conduction, as in a furnace. When a flame is used the glow occurs within the flame only.

(4) In the case of photo-luminescent substances the lower limit of temperature of flame excitation is often, but not always, above the point at which ordinary photo-excitation ceases.

(5) The active range in general extends above that at which thermo-luminescence occurs.

(6) *Not all flames are effective;* in fact, the hydrogen flame, and to a lesser degree flames containing hydrogen such as the colorless flame from ordinary illuminating gas is, so far as known, the sole source of this type of excitation. Flames from alcohol, ether, and carbon disulphide were found to be *inactive.*

(7) The effective region may be described as the outer portion of the reducing zone of the flame. This zone may be readily and very strikingly located and observed by allowing the flame to impinge upon a red-hot copper surface. The coating of oxide on the copper is then reduced to metallic form throughout a perfectly defined and sharply bounded region within the flame, the reduced area being distinguished by the marked change in reflecting power and emissivity. The identification of the region of activity with the edge of this reducing zone is therefore very simple.

Temperatures were estimated in these experiments by placing the substance in the form of a fine powder on one of the end faces of a massive cylindrical block of copper about 30 mm. in diameter and 20 mm. thick. A narrow slot in this face received a platinum wire, the copper being hammered down so as to grasp the wire and make it a part of the surface. This copper-platinum contact formed one junction of a thermo-electric element by means of which the temperature of the face of the block could be measured. As we have been unable to find data giving directly in millivolts the E. M. F. of such a copper-platinum junction, we insert here for the benefit of those who may have occasion to use this very convenient means of measuring temperatures to 1000° C. the results of our calibration.

TABLE LII—*Millivolts and temperature differences of copper-platinum thermo-element*

[M.V. = millivolts: t = temperature of hot junction in degrees centigrade—the cold junction being at 0° C.]

t.	M.V.	*t.*	M.V.	*t.*	M.V.	*t.*	M.V.
°C.		°C.		°C.		°C.	
25	0.210	275	2.640	525	7.180	775	14.440
50	.425	300	2.850	550	7.780	800	15.075
75	.640	325	3.330	575	8.400	825	15.770
100	.855	350	3.750	600	9.020	850	16.490
125	1.069	375	4.170	625	9.900	875	17.320
150	1.282	400	4.610	650	10.820	900	18.220
175	1.497	425	5.060	675	11.640	925	18.580
200	1.707	450	5.600	700	12.410	950	18.940
225	1.916	475	6.110	725	13.120	975	19.360
250	2.235	500	6.076	750	13.820	1000	19.760

To insure snugness of contact between the luminescent substance and the copper, the face of the block was variously grooved and slotted and in some instances the powder was applied by smoking the block in fumes of a burning metal or over an electric arc, into which the oxide or some salt of the substance under investigation had been introduced. Above 550° temperatures could likewise be determined with the Morse thermo-gage, using a calibration of that pyrometer, previously made, and these determinations agreed perfectly with the indications of the thermo-element. The copper block was bored through axially and the hole, 1 cm. in diameter, afforded a surface which could be coated and which gave a fair approximation to black-body conditions. It was sometimes advantageous to compare the appearance of coatings thus inclosed with those on the open end of the block.

Much attention was given to the difficult question of the difference of temperature between the upper surface of the coatings and the surface of the metal on which they were mounted. Obviously, the face of a poorly conducting layer would be cooler than the hot block when out of the hydrogen flame and hotter than the underlying metal when in the flame and it was important to estimate this difference and to know that it could be neglected.

That the difference was small in most cases where the precise temperature was in question we were able to show in many ways.

If, for example, a coating of one of the sulphides which glows strongly with a green or blue color at a temperature just below the red heat be scattered loosely and with varying thicknesses on the brass gauze or the copper block and excited in the manner already described, it is easily possible to render the thickest parts of the coating red hot and non-luminescent, while thinner regions within the flame, owing to cooling effects of the metal beneath, are below the red heat and strongly luminescent. If, now, the thinner regions of the coating coincide in color and brightness with the very thinnest and therefore with the underlying metal, one may feel assured that temperature measurements of the metal surface will apply up to a certain thickness of coating and even estimate approximately at how many hundredths of a millimeter thickness the departure of the temperature of the surface of the metal will become noticeable. It was found that for thicknesses under 0.1 mm. the departure was not of a size to appreciably vitiate our estimates, but that at greater thicknesses it rapidly became significant.

In general, estimates of temperature were made with the massive copper block, heated by an electric furnace or a Bunsen flame. Its mass and conductivity were such that the small hydrogen flame applied from above had no measurable effect on the surface, *i. e.*, no

effect that could be noticed with the Morse gage. The only difficulty, therefore, was with local heating of the upper layers of the powdered coatings. The above-mentioned estimate of the permissible thickness of coatings was confirmed by observations of the heating power of the flame on layers of black oxides the radiating power of which rendered it possible to determine their temperatures directly with the pyrometer. Thus we were able to assure ourselves that for the thicknesses of coating used when temperature measurements were involved the temperature of the surface of the copper coincided with sufficient exactness to that of the luminescent coating. The most satisfactory direct check, on the whole, consisted in substituting for the luminescent powder a coating resembling it as nearly as possible in all other physical characteristics and to observe its appearance in and out of the flame and different zones of the flame. Since under the conditions of our experiments the brightness of these regions was appreciably the same, it seemed altogether reasonable to assume that the luminescent surfaces in the study of which we were engaged had approximately the same temperature as the copper block or metal gauze upon which they rested.

In further support of this assumption,[1] the following observation may be cited: From one end of a cylindrical copper block about 5 cm. long and 2.5 cm. in diameter, a hole about 0.5 cm. in diameter and 4 cm. in depth was bored parallel to the axis. When the block was suspended over a large Bunsen burner and heated to uniform incandescence, the appearance of the end with the hole was as follows:

(1) With the flame adjusted so as to maintain the surface of the copper in a reduced metallic state, the aperture, because of the radiation under black-body conditions from within, appeared as a cherry-red disk on a very dark background.

(2) With the flame shifted so as to oxidize the surface of the copper, the radiation from the end of the rod was so nearly equal to that from the hole that the latter was *just barely perceptible.*

(3) The flame having been extinguished and a small portion of the oxidized surface contiguous to the hole having been moistened with a solution of uranium chloride, the block was again heated to incandescence. It was now observed that in the oxidizing flame the patch to which the uranium chloride had been applied and which was now covered with a very thin layer of uranium oxide was scarcely to be distinguished from the surrounding surface *or from the hole.* In the reducing flame, however, this patch, which was not reduced by the flame, stood out against the much weaker radiation from the metallic copper, and, so far as could be judged by the eye,

[1] E. L. Nichols. Phys. Rev. XXV, 380, 1925.

was almost of the same brightness and color as the hole, from which it could be distinguished only by its shape. Settings with the optical pyrometer when the block was at 870° C. confirmed the judgment of the eye, the relative brightness being as follows: hole, 1.00; CuO, 0.954; uranium oxide, 0.954; metallic copper 0.14. The value for copper is what one would expect, being intermediate between that given for the green (0.17) and for the extreme red (0.09).[1]

Of the essential equality of the two oxides, quite aside from the above measurement, there can be no doubt in the mind of one who has seen them side by side upon the incandescent surface, nor of their approximately complete blackness to one who has viewed them by reflected light at a temperature of 500° or more. The last-named observation was checked by measuring the melting-point of minute crystals of KCl placed upon the incandescent oxide. The pyrometer, using the calibration given by the Bureau of Standards, yielded the accepted melting-point within 3° C. when the settings were made upon the uranium oxide. It will be understood that these very high values of relative emissivity apply only to oxides formed by the hydrogen flame in the manner described and used practically in the nascent state, and not necessarily to these two substances in general.

This conclusion was indirectly verified in subsequent studies of cathodo-luminescence at high temperatures, in which it was found that the temperatures at which calcium oxide and other substances ceased to be active under cathode bombardment were the same as the extinction temperature estimated in the present investigation.

Experiments with electrostatic fields—Deeming it highly probable that the effect in question involved ionization or the production and movement of charged particles, electrostatic fields were brought to bear with lines of force transverse to the stream-lines of the flame and also parallel to the same. Although potential differences of many kilovolts were thus applied, *no result whatever could be observed.*

Photo-excitation at high temperatures—To test as thoroughly as possible the suggestion that flame excitation may be due to ultra-violet radiation within the flame itself, very powerful photo-excitation was applied to certain of our substances at high temperatures. To this end a mercury arc lamp was made of the form shown in figure 109. Above the arch of the inverted U-tube which contained the arc a vertical tube, *T*, was inserted. This had a glass stopper to which a body (*S*) to be subjected to radiation from the arc could be suspended so as to hang within the path of the discharge. Various substances which were excited by the flame were thus treated; *e. g.*, calcium oxide, zirconium oxide, etc. These remained completely

[1] Burgess. Trans. of le Chatelier on Measurement of high temperatures, p. 497.

inert, whereas a synthetic ruby under like conditions was exceedingly brilliant until it reached its temperature of extinction, when it was suddenly quenched. It seemed highly improbable that any photo-excitation by the hydrogen flame could approach that of this mercury arc in intensity.

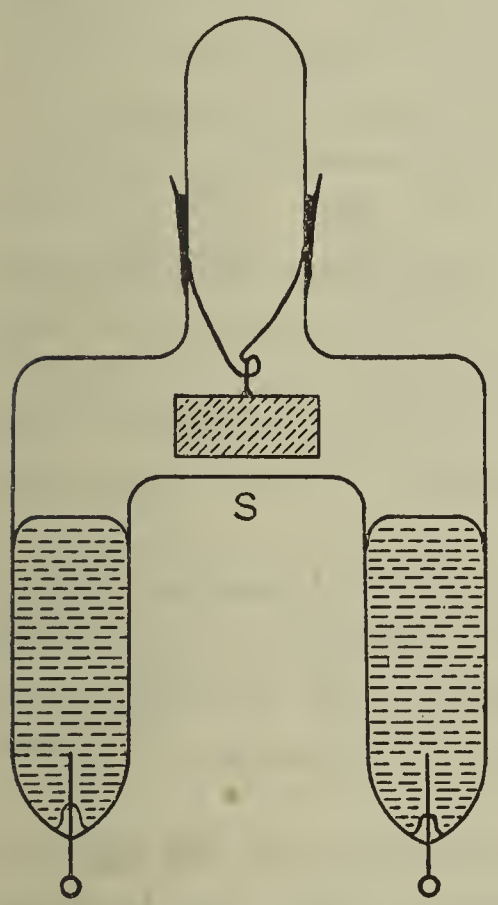


FIG. 109—Mercury arc for excitation at high temperatures

Combustion a necessary factor—This fact is very prettily brought out in an experiment based upon a method described by Simonini[1] and used by him in the study of the luminous properties of gas-mantles.

A glass tube about 1 cm. bore and 20 cm. in length was coupled to the nozzle of an oxy-hydrogen blast-lamp as in figure 110. A small amount of calcium oxide was distributed within the tube from end to end, coating the inner walls thinly.

When hydrogen was run through the tube and ignited at the free end (*F*) there was no excitation of the calcium oxide, even though the tube was heated to a dull red. The addition of air admitted through the oxygen intake likewise produced no effect, whatever the temperature, until the supply of oxygen within the tube caused the flame to "strike back." When this occurred the progress of the flame through the tube could be traced by the luminescence of the oxide.

By adjustment of the supply of oxygen the zone of combustion (*Z*) could be brought to rest within the tube, and its position was then clearly marked by a narrow ring of luminescent powder.

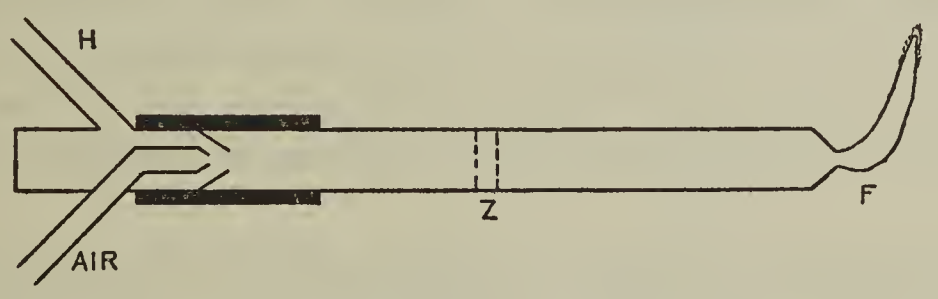


FIG. 110—Tube for excitation in the combustion zone

From these observations it appears:

(1) That luminescence is not produced by the mere presence of hydrogen, at temperatures up to the red heat.

(2) That hydrogen and oxygen mingled as above have no effect.

(3) That where combustion occurs luminescence is produced, but then only in the narrow zone where the reaction is in progress.

[1] A. Simonini. Trans. Illuminating Eng. Soc., 1909, p. 648.

In the hydrogen flame we have, besides the combination with oxygen, the production of H_1 or H_3 or both, as has been shown by Langmuir,[1] by Wendt,[2] by Wood,[3] and by others.

It might reasonably be suspected that disturbances incident to return of these unstable forms to H_2 would produce the phenomenon of luminescence in substances with which the gas was in contact. If so, the atomic hydrogen would presumably be swept along with the flow of gas in the experiment just described and the luminescent zone extended, with decreasing intensity, for some distance from the boundary between oxygen and hydrogen within the tube. That, however, was not the case, and it was found by numerous modifications of the experiment that the active zone was equally sharp and well defined, whether combustion occurred by igniting a jet of hydrogen in oxygen or vice versa. The luminescence always occurs, however, *within the hydrogen* next to the boundary between hydrogen and oxygen.

Experiments with hydrogen-filled tubes at various pressures, within which it was attempted to produce atomic hydrogen by powerful electric discharges, both direct and alternating, and to expose our luminescent oxides to this gas when heated to a wide range of temperatures, were all equally without result.

The evidence at present therefore appears to be against the assumption that the presence of H_1 or H_3 in contact with the luminescent materials is the cause of the effect which we have called flame excitation.

ACTIVE AND INACTIVE MATERIALS

Some of the materials sensitive to flame excitation, in addition to the old line already mentioned, are:

(*A*) Calcium oxide from various sources, zirconium oxide, magnesium oxide, silicon oxide, aluminum oxide, zinc oxide.

(*B*) Certain phosphorescent sulphides such as Sidot blende and Balmain's paint and sulphides of the Lenard and Klatt type.

Not all the Lenard and Klatt preparations are active. Out of 44 tested the twelve given in table LIII, responded strongly, a few others dimly.

(*C*) In addition to the above, white sapphires, corundums, synthetic rubies, and crystals of calcite, fluorite, kunzite, and topaz responded to the flame excitation, as did boric acid, telluric acid, and very pure samples of cadmium phosphate, calcium carbonate, calcium sulphide, and zinc sulphide, all incapable of photo-excitation. On the other hand, all dark-colored substances tried, such as the oxides of copper, lead, iron, nickel, manganese, cobalt, cadmium, tungsten, etc., were

[1] Langmuir. J. Am. Chem. Soc., 38, 1145, 1916.
[2] Wendt and Landauer. J. Am. Chem. Soc., 42, 930, 1920.
[3] Wood. Phil. Mag., 44, 536, 1922.

inert. So likewise were the oxides of bismuth, antimony, barium, and strontium; samples of the oxides of erbium, cerium, lanthanum, and thorium; materials from a freshly ignited Welsbach mantle and from a Nernst filament and specimens of uranium glass, didymium glass, fused quartz, etc.

TABLE LIII—*List of Lenard and Klatt sulphides that responded strongly to flame excitation*

Compound	Excitation	Color	Brightness	Spectrum
No. 3 CaS, Bi, Na_4BO_4	Photo- Thermo- Flame-	Blue-violet Deep blue Blue-white	Very bright Very bright Very bright	Green to violet
No. 5 CaS, Mn, NaF	Photo- Thermo- Flame-	Yellow Absent Yellow-green	Dim ..... Very bright	Red to green (no violet)
No. 9 SrS, Bi, K_2CO_3	Photo- Thermo- Flame-	Blue-green Very dim Blue-green	Bright ..... Bright	Green to blue (no red)
No. 27 CaS, Sb, NaF	Photo- Thermo- Flame-	Blue-green Dim Blue-green	Medium ..... Very bright	Green to blue (no red)
No. 29 CaS, Pb, NaF	Photo- Thermo- Flame-	Green Absent Pale green	Very dim Absent Very bright	Green to blue (no red)
No. 32 CaS, Cu, LiF	Photo- Thermo- Flame-	Blue ..... Blue-green	Bright Absent Medium	
No. 34 CaS, SrS, Bi, NaF	Photo- Thermo- Flame	Blue ..... Deep violet	Bright Absent Moderate	
No. 36 CaS, SrS, Bi, Na	Photo- Thermo- Flame-	Blue ..... Blue-green	Medium Very dim Bright	Blue to green (no red)
No. 38 CaS, SrS, Bi, Na	Photo- Thermo- Flame-	Blue ..... Blue-green	Medium Absent Bright	
No. 39 CaS, SrS, BaS, Cu, Bi, LiF	Photo- Thermo- Flame-	Yellow-green ..... Pale yellow	Medium Absent Medium	
No. 43 CaS, Bi, Cu, CaF	Photo- Thermo- Flame	Blue-green Blue-green Blue-white	Bright Very bright Bright	
No. 44 CaS, Bi, Sb, Na	Photo- Thermo- Flame-	Blue ..... Pale green	Medium Absent Very bright	Blue to green (no red)

Calcium tungstate, one of the most brilliant of fluorescent substances under the action of X-rays, is quite inert when subjected to the hydrogen flame as is artificial willemite, which is perhaps the brightest of photo-luminescent bodies.

II. THE ACTIVE OXIDES

Calcium oxide, whether obtained from the slaked lime mentioned above or from calcite crystals or by burning metallic calcium, gave the same strong yellow glow in the hydrogen flame and the various preparations were active through the same range of temperature. Complete extinction occurred for all these samples at about 690° C.[1] Since the oxide from these varied sources was equally and similarly active, it does not seem probable that the effect depends on the presence of small amounts of an accidental impurity, as has been shown[2] to be the case in the photo-luminescence of Franklin Furnace calcites.

Such admixtures, however, may modify the character of the glow. Thus, a specimen of calcium oxide to which a trace of a bismuth salt had been added, with subsequent heat treatment, showed a brilliant *blue-green* fluorescence instead of the usual *yellow,* when excited by the hydrogen flame.

Of *zirconium oxide,* the preparations available were some old disks from a Linnemann[3] "zircon-light" apparatus[4] and a purified white oxide in powdered form from the Cornell Department of Chemistry.

In the hydrogen flame the Linnemann disks gave a remarkable deep red and in cooler portions a pale blue-green fluorescence. The white powder showed the blue-green only.

The red fluorescence is probably due to some impurity, but apparently not to the boric acid used as a binder. At least, admixture of the latter with pure oxide failed to impart even a suggestion of a ruddy tone to the glow in flame or in vacuo.

To estimate the active range of luminescence, part of a disk was pulverized and strewn on the surface of the cold copper block in the usual manner. The observed phenomena were as follows:

(1) Pale blue-green fluorescence which began very definitely when the block was heated to 76° C. It remained visible until the upper limit of temperature was reached at 372°. Throughout this entire range of temperatures there was no suggestion of the red luminescence, but on heating to a dull red we saw:

(2) The deep-red luminescence already described.

Lower limit	440°
Upper limit	720°

[1] To be more precise, it should be stated that the luminescence spectrum consists of two or more overlapping bands. One of these, lying chiefly in the red-yellow, begins to respond to flame excitation at a lower temperature than the other and vanishes at about 670°. The other band, which is yellow-green, becomes visible only at higher temperatures and does not disappear altogether until the oxide reaches a temperature of 725°. Details of the experiments on which this statement is based are given in section II of this chapter.

[2] Nichols, Howes and Wilber. Physical Review (2), XII, p. 35, 1918.

[3] Linnemann, Dingler's Journal, CCLX, p. 218.

[4] The disks, according to Erdmann (Chimie, p. 139), were prepared by moistening zirconium oxide ("Zirkonerde") with a solution of boric acid, compressing, and baking. Such disks were used by Rubens and others as sources of infra-red radiation.

On account of the ruddy color, there was some difficulty in distinguishing with certainty between this luminescence and ordinary red heat, but its temperatures of appearance and vanishing were fixed and definite and the color was quite different from that of a red-hot body, being more nearly of the approximately monochromatic tint which one gets through ruby glass.

Silicon oxide, whether in the form of a precipitated powder or a smoked coating sublimed in the arc from metallic silicon or from quartz, exhibits a pale green-white, nearly white fluorescence in the hydrogen flame. Quartz crystal, not crushed, is difficult of excitation and fused quartz appears to be inactive.

To determine the temperature range, a very thin coating of the precipitated silica was rubbed into the surface of the copper block. Inactive at room temperature, the fluorescence came very suddenly into view on heating the block. The threshold was very sharp and definite, so much so that a drop of cold water applied to the surface of the block 2 cm. away would immediately extinguish the luminescence within the flame on the side nearer the drop by the slight local fall in temperature thus temporarily produced. The range of temperatures was found to be

Lower limit	85°
Upper limit	367°

Aluminum oxide in the form of a fine powder from the department stock-room was notable for the very low temperature at which it began to glow. The temperature range for the pale-green fluorescence was:

Lower limit	52°
Upper limit	692°

At higher temperatures this coating when in the active zone of the flame presented a curiously mottled appearance, there being patches of reddish hue, others green-blue, and others nearly white. This strange mosaic might have been ascribed to a lack of homogeneity in the material used but for the fact that another coating obtained from the smoke of burning aluminum was similarly variegated under cathode bombardment. It seems to be a general property of this oxide and is under detailed investigation.

Aluminum oxide in crystal form was found likewise to be susceptible to flame excitation. A synthetic ruby gave a greenish glow without a trace of the well-known deep-red photo- and cathodo-luminescence. A white sapphire, known to be synthetic, fluoresced a very delicate pale green in the active zone of the flame, although it, like the ruby, glowed red under cathodo-excitation.

Magnesium oxide obtained by smoking the copper block in the fumes of burning magnesium wire showed a fine white flame-fluorescence:

Lower limit	76°
Upper limit	680°

Magnesium carbonate, the ordinary compressed pharmaceutical preparation, showed a similar white fluorescence, and since the limits were practically the same as for the oxide (76° to 670°), it may well be that there is partial decomposition of the carbonate to oxide, as in the case of the calcite referred to in a subsequent paragraph.

At temperatures much higher than the above, blended with the brilliant white selective radiation from magnesium oxide, there is another stage of luminescence, blue-violet in color, the exact temperature relations of which are difficult and have not yet been determined.

Zinc oxide, like the oxides of zirconium and magnesium, exhibits two stages of flame luminescence, but in this case the lower stage is somewhat difficult to bring out. The color of the luminescence is an intense red. It begins at 568° and above 700° (704°) it goes over into a higher stage characterized by a blue-green glow which persists to 948°. The total range for both bands is thus:

Lower limit	568°
Upper limit	948°

The green glow is brilliant and so strikingly different in hue from the temperature radiation on which it is superimposed that it admits of very definite quantitative study.

An account of these measurements and of observations on the more difficult higher stage luminescence of magnesium oxide is presented in Chapter X.

Titanium oxide, when in contact with the hydrogen flame, shows a very feeble grayish blue luminescence. If, now, the copper block be progressively heated, this will be supplanted by a deep-red luminescence at a temperature somewhat below the beginnings of incandescence. This grows brighter as the temperature rises and is easily visible superimposed upon the bright incandescence of the copper, from which it is distinguishable by its pure-red color. At a still higher temperature the luminescence changes to yellow. The maximum brightness is clearly passed before the temperature of 800° is reached. The glow continues to be visible, however, almost up to the melting-point of copper. On cooling, the transition from yellow to red is very sudden. It was located at 677°. The red band in its turn disappeared at 425°. We have, then, three distinct outcroppings of luminescence: (1) gray-blue (very feeble), from

room temperature to 425° C; (2) red (strong), 425° to 677°; (3) yellow (strong), 677° to about 1000°.

Germanium oxide—Like the closely related oxide of titanium (TiO_2), germanium oxide is not luminescent under the action of the iron spark. When brought into contact with a hydrogen flame, however, it is feebly excited within the active zone of the flame. The glow is a pale blue-green in color and barely perceptible. At a temperature below that of incandescence, this faint luminescence is supplanted by a much stronger ruddy glow, quite like that which is observed when TiO_2 is similarly treated. The luminescence might now be easily mistaken for ordinary incandescence but for its color, which is an almost pure red, and for the fact that it is confined to the active zone of the flame. The subsequent change to a yellow luminescence, which occurs in the case of titanium oxide at 677° C., has not been observed, perhaps because germanium oxide in the hydrogen flame begins to darken before that temperature is reached.

OXIDES SUBLIMED IN THE ELECTRIC ARC

In the course of the foregoing experiments various methods were used to produce thin films of the substances to be investigated. One method was to place a small quantity of the metal, or of one of its salts, in the crater of a direct-current carbon arc and to collect a layer of the finely divided oxide on a metal strip or disk held in the smoke-laden convection current. The first films thus obtained were of calcium oxide, and these under cathode excitation showed the same fine yellow glow already observed in the study of flame excitation. It seemed desirable, therefore, to determine what other oxides lent themselves to this method of preparation and to learn something of their luminescent properties.

Of the films prepared in the course of our investigation the oxides of the following metals were notably active: calcium, magnesium, zinc, zirconium, silicon, aluminum. The luminescence of oxides of lead, boron, barium, and strontium was very dim. All other oxides tested, including those of cerium, thorium, titanium, copper, manganese, bismuth, cadmium, and uranium were inactive. Since the results obtained with these films have an important bearing upon the relations of flame excitation and cathodo-excitation and also upon the probable nature of both processes, we give them in some detail here.

The active films were found to have the following characteristics in common:

(1) They are not photo-luminescent at ordinary temperatures.

(2) They continue to fluoresce, under cathode bombardment, at temperatures far above those at which, in general, photo-luminescence becomes extinct.

(3) They are all capable of flame excitation as well as of cathode excitation.

(4) None of the oxides thus prepared show notable persistent phosphorescence, although most of them with small admixtures of chromium, manganese, or bismuth, by suitable heat treatment, may be rendered strikingly phosphorescent. This is particularly true of certain preparations of Al_2O_3 with traces of chromium.

(5) With rise of temperature, changes in the color of the luminescence occur which correspond in general with those observed by

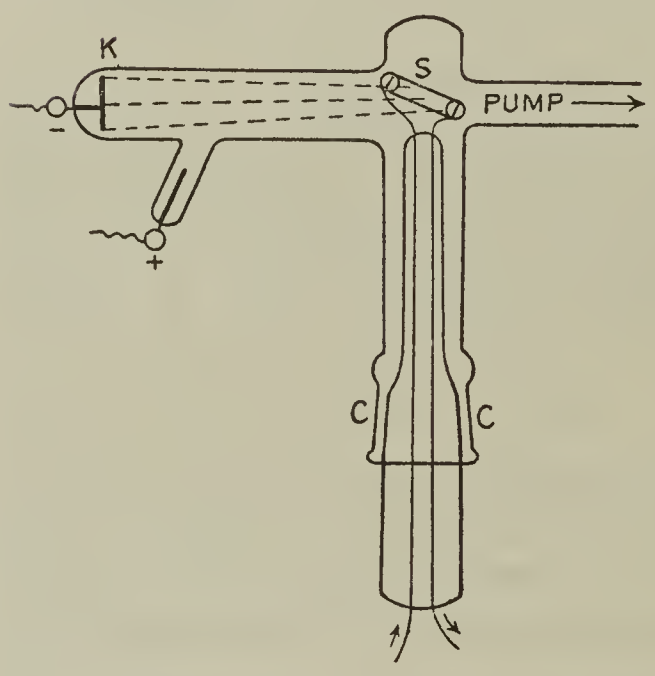


FIG. 111—Vacuum-tube for cathodo-luminescence at high temperatures

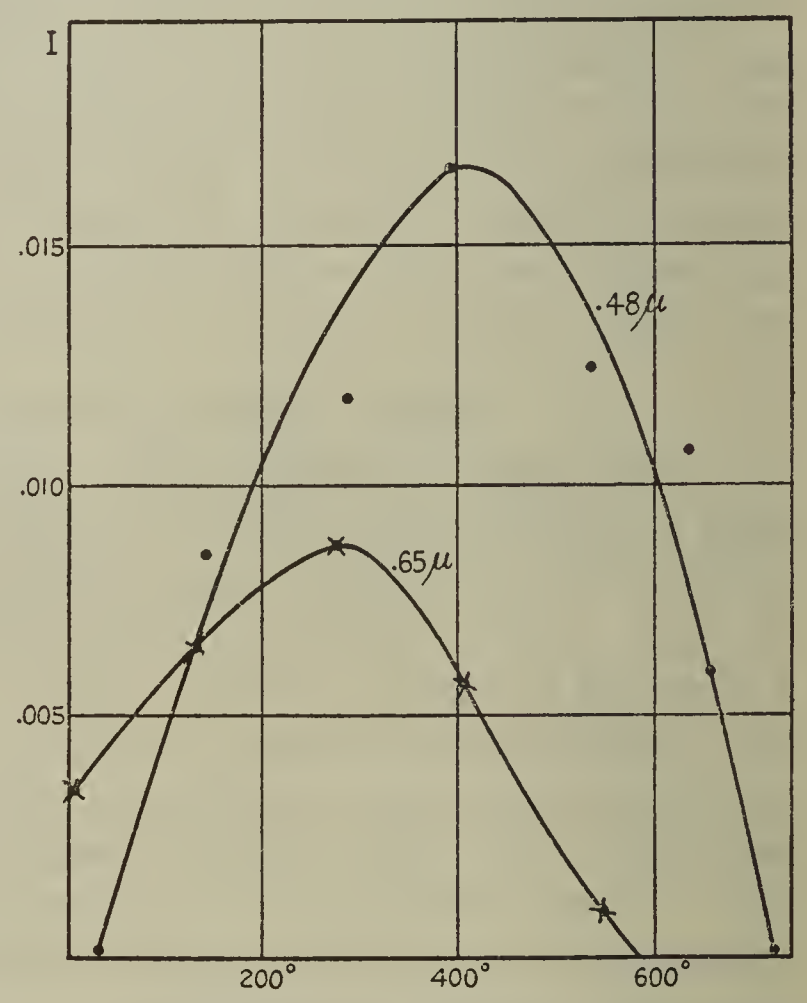


FIG. 112—Brightness of the red (65μ) and the blue-green (48μ) in the cathodo-fluorescence of CaO at various temperatures

Goldstein,[1] Crookes,[2] and by Wiedemann and Schmidt.[3] Both Goldstein and Crookes noted the change of the cathodo-luminescence of calcium compounds from yellow toward a blue on heating. Wiedemann and Schmidt, in a systematic investigation of the effect, showed that the color-shift towards violet was common to numerous substances which they tested up to the temperature where the glass of their vacuum-tubes began to soften.

UPPER TEMPERATURE LIMIT OF CATHODO-LUMINESCENCE

To estimate the temperature at which luminescence under the excitation of the cathode-rays ceases, a vacuum-tube of the form shown in figure 111 was prepared. By means of the terminals

[1] Goldstein. Wien. Ber., LXXX, p. 15.
[2] Crookes. Proc. Royal Soc., 1881, p. 209.
[3] Wiedemann and Schmidt. Wiedemann's Annalen, 56, p. 218.

through the ground-glass stopper at *CC*, a strip of thin nichrome ribbon, *S*, could be mounted so as to expose the oxide with which it was coated to bombardment from the cathode *K*. The strip was heated by an electric current and its temperature in vacuo was determined in terms of the current. The calibration was made by means of the melting of various selected salts placed in the form of fine powders upon the surface of the strip and these temperatures were checked, above the red heat, by the use of an optical pyrometer (the Morse thermo-gage).

The extinction of the cathodo-luminescence was quite sharply marked when the nichrome strip with its coating was gradually heated, especially in the case of substances having a greenish or blue fluorescence which was in contrast with the red heat of the background. For calcium oxide, from whatever source sublimed, the temperature of extinction as observed directly with the eye was always the same, *i. e.*, 690° C. This temperature, as was shown on a previous page, is *identical with that of the extinction of luminescence under flame excitation.*

By observing the glowing strip with the Morse thermo-gage, we could measure the equivalent "black-body" temperatures of the coating at various actual temperatures of the strip.

It had been established in the course of the studies already described in this chapter that the spectrum of the luminescent calcium oxide, like that of the calcites[1] from Franklin Furnace, has two broad, complex, overlapping bands. In our pyrometer readings we therefore used a red screen (equivalent wave-length 0.65μ) and a blue-green screen (equivalent wave-length 0.48μ) and were thus able to study the behavior of the two bands almost independently.

Observations of the color-changes showed that the red band began to fall off in brightness at lower temperatures than the green, and this was readily confirmed by watching the spectrum as the temperature rose. In spite of the overlapping of the two bands, their independent growth and decadence was very striking.

The curves in figure 112 indicate roughly (the irregularities being chiefly due to lack of accurate control of the vacuum) the rise of the two curves to a maximum of brightness, and their subsidence at the higher temperatures. It will be noted that the red band reaches its maximum at about 280°, at which temperature it has more than double the brightness observed at 20° C. The green band is not visible at 20°. It attains its maximum at about 425°. Relatively speaking, red is predominant at the lower temperatures; green increasingly so from 150° upward. The pyrometer is apparently more sensitive than the unaided eye in detecting luminescence super-

[1] H. L. Howes. Phys. Rev. (2), 17, 1921, p. 460.

imposed upon temperature radiation. Thus, the disappearence of the green band is found to lie somewhat above 700°, at which temperature it appears to have vanished, so far as direct visual observation goes.

It is of interest to compare figure 112 with figure 18 of the chapter on the fluorescence of calcites, etc.,[1] where the same relative increase of the brightness of the shorter wave-lengths with rising temperatures is apparent.

TABLE LIV—*Temperatures and luminous intensities of calcium oxide*

Temp. of strip	Red screen		Green screen	
	Black-body temperature	Intensity[a] of luminescence	Black-body temperature	Intensity of luminescence
°	°		°	
20	680	0.0040	.....	0.0000
150	702	.0067	712	.0083
280	712	.0083	723	.0104
410	695	.0055	744	.0170
542	644	.0010	726	.0113
650	.....	.....	723	.0094
675	666[b]	.0000	710	.0044
725	.....	.....	690[b]	.0000

[a] Intensities here, as elsewhere, except where otherwise noted, are in terms of that of a black body at 1000° C.

[b] Note that after the disappearance of luminosity the "black body" temperature is less than the indicated temperature of the strip. This is to be expected in the case of a metallic surface coated with a whitish powder.

LOSS OF PHOSPHORESCENCE BY HEATING

One of the striking differences between the behavior of CaO sublimed in the arc and the calcite from which it is derived is in the loss of phosphorescence.

Calcite from Franklin Furnace was powdered and sifted upon the surface of the nichrome strip, using powdered resin as a binder.

When cold this preparation glows in the cathode tube with the well-known orange-yellow luminescence, not easily distinguishable from that of CaO at the same temperature. It has, however, persistent phosphorescence of long duration. On exciting at higher temperatures, step by step, we find the phosphorescence continuing up to 475°. Above 185°, however, the color of the after-glow is *white* instead of *red,* and even at lower temperatures the red phosphorescence changes to white during decay.[2] The white phosphorescence grows rapidly dimmer above 325°, but is still persistent, being easily observable for several seconds. Above 475° persistent phosphores-

[1] Chapter II, fig. 18.

[2] Nichols, Howes and Wilber. Phys. Rev. (2), XII, p. 351.

cence is not observable. We made no tests for phosphorescence of the vanishing type.

The fluorescence of this preparation ceased at the usual temperature already established for calcium preparations, *i. e.*, 690°. The substance regained its phosphorescent properties on cooling, so long as it was not heated much above this temperature; but on heating for some 15 minutes at 900° it underwent a permanent change—probably loss of CO_2—and became non-phosphorescent even at room temperatures. It was now indistinguishable from our CaO prepared in the arc, its luminescence going over from orange to green-yellow on heating and being quenched at 690°.[1]

EFFECT OF PRESSURE

In the course of our experiments we noted that the oxide under observation often began to glow under cathode bombardment at relatively very high pressures, reached its maximum at a moderate vacuum, and declined almost to extinction at the lowest pressures reached. That the luminescence at the higher pressures, where the glass of the tube had not begun to glow, was of cathodic excitation and not due to ultra-violet radiation was readily determined by the use of a magnet.

By placing in the same tube a coating of CaO, a crystal of calcite, and a synthetic ruby, it was found that the oxide was in distinct luminescence during the earlier stages of pumping, while the ruby and calcite were still dark. These, however, which began to glow at somewhat lower pressures, soon greatly exceeded the oxide in brightness and continued to increase as the vacuum improved, whereas the oxide reached a maximum of intensity and fell off to relative inactivity. Similar effects were observed with ZrO_2, SiO_2, and Al_2O_3.

To make these observations more definite without going into troublesome refinements, a spark-gap with nickel-plated balls 25 mm. in diameter was mounted in parallel with the terminals of the tube and observations of the brightness of luminescence of the coating were made with the Morse thermo-gage, for various sparking distances. The discharge through the tube during these measurements was obtained from a large four-plate Toepler-Holtz machine.

Any considerable accuracy was difficult, owing to the prevailing atmospheric conditions, to unstable states of vacuum within the tube, and the rather rapid decline in the activity of the coatings, which were modified and destroyed by the cathode rays. It was found possible, however, to establish in a semi-quantitative manner the relations between tube voltages and luminescence for films of CaO, ZrO_2, and SiO_2. By way of check similar measurements were made upon the cathodo-luminescence of a synthetic ruby.

[1] See further the chapter on Types of Phosphorescence (Chapter VI).

The indications of the spark-gap were converted into kilovolts by means of curves plotted from measurements by Peek[1] of the relation between spark-gap and voltage. The applicability of his data to the conditions of our experiment was verified by the use of a Braun electroscope.

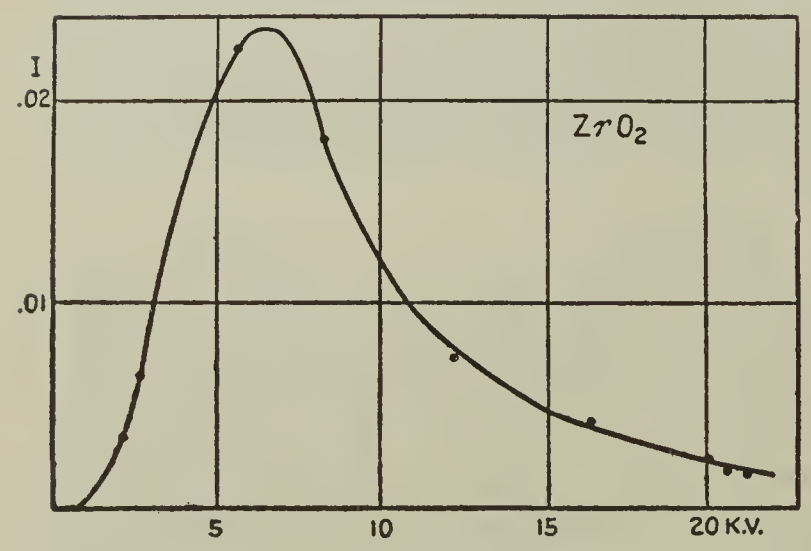


FIG. 113—Brightness of the cathodo-luminescence of ZrO_2 at various pressures

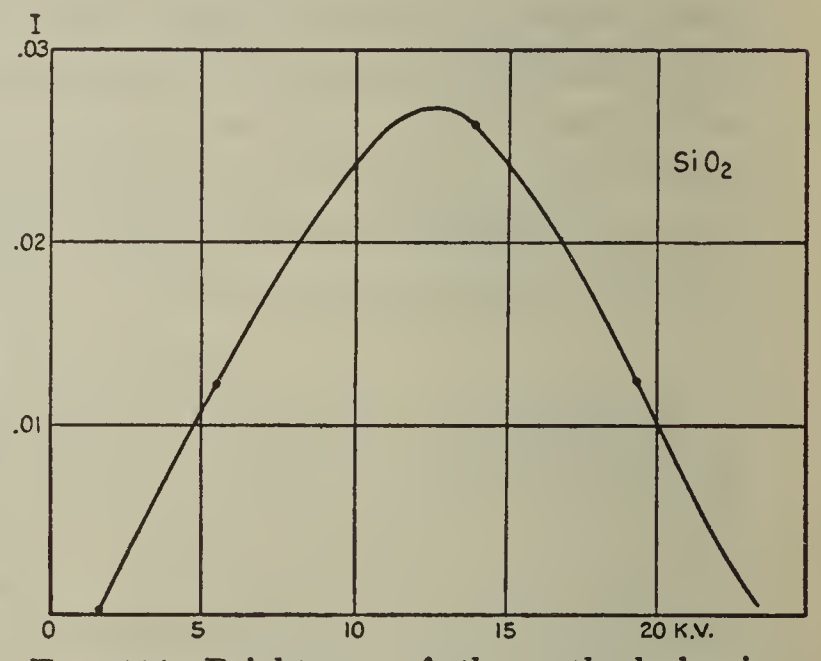


FIG. 114—Brightness of the cathodo-luminescence of SiO_2 at various pressures

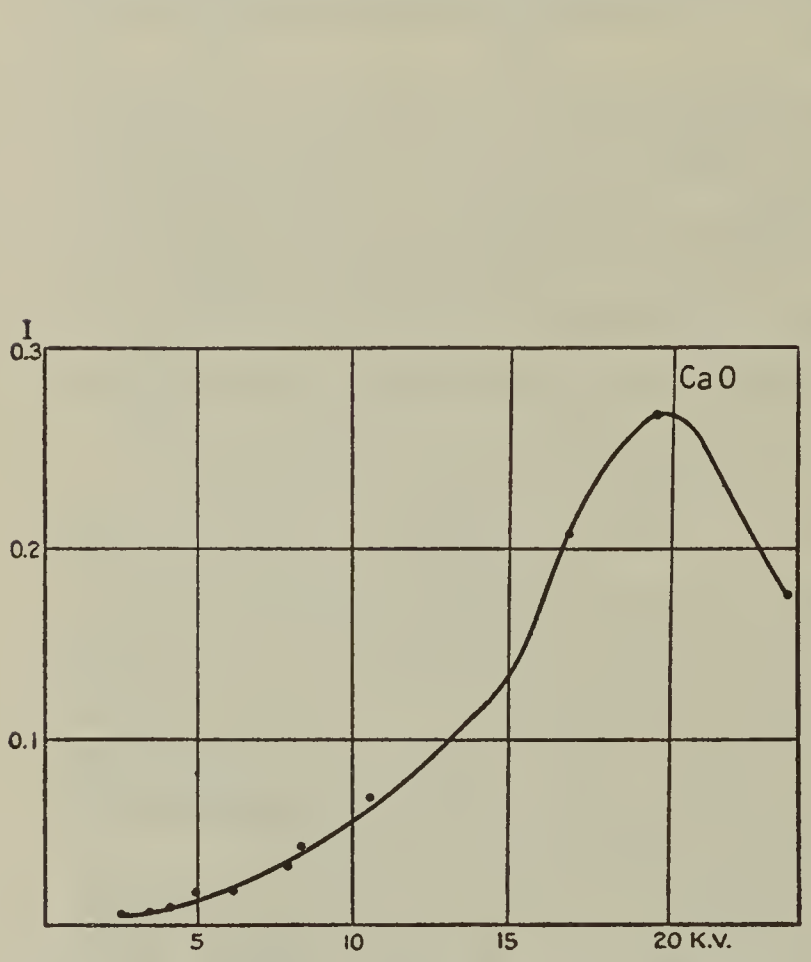


FIG. 115—Brightness of the cathodo-luminescence of calcium oxide at various pressures

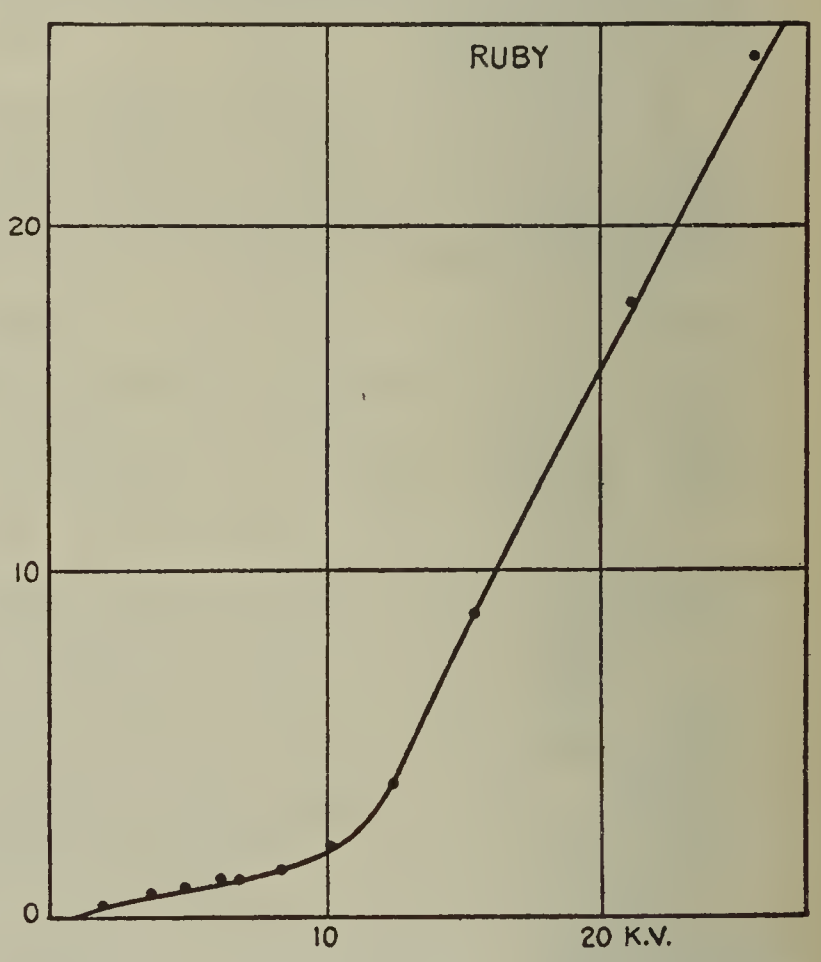


FIG. 116—Brightness of the cathodo-luminescence of a synthetic ruby at various pressures

The results of our observations are given in table LV and figures 113, 114, and 115, and for the ruby, in table LVI and figure 116. It appears from these curves (figs. 113, 114, 115, and 116) that there is a well-marked maximum for each coating beyond which the bright-

[1] Peek. Dielectric Phenomena, p. 87.

ness falls off—a fact which agrees with the visual observations already mentioned. This maximum occurs at the vacuum corresponding to 6 kv. for ZrO_2, 11.5 kv. for SiO_2, and 20 kv. for CaO. Rejuvenation of the glow could be produced at will by pumping until the maximum of brightness was passed and then admitting a small amount of gas to the tube. This brightening up was especially striking in the case of coatings of silicon dioxide.

TABLE LV—*Cathodo-luminescence of three oxides at various tube voltages*

Substance	Kilovolts	B. B. temp.	Intensity
		°C.	
Calcium oxide.....	0.8	620	0.0009
	2.1	666	.0026
	2.6	670	.0029
	3.1	726	.0112
	5.0	735	.0142
	6.6	728	.0120
	8.5	764	.0257
	8.9	794	.0430
	10.4	819	.0750
	17.3	872	.1860
	20.2	894	.2650
	24.9	874	.1680
	26.2	861	.1580
Zirconium oxide.....	2.4	686	.0046
	3.0	710	.0080
	5.1	756	.0220
	8.0	750	.0182
	12.3	700	.0061
	17.7	683	.0043
	20.3	675	.0034
	20.9	654	.0025
	21.8	639	.0015
Silicon oxide.....	1.4	.....	.0000
	5.2	728	.0120
	13.5	765	.0262
	18.4	733	.0135

TABLE LVI—*Cathodo-luminescence of the ruby at various tube-voltages*

Kilovolts	Black-body temp.	Intensity
	°C.	
0.8	....	.....
1.7	700	0.0061
2.3	776	0.032
3.6	792	0.045
5.0	834	0.097
6.6	850	0.133
8.5	865(?)	0.140
10.3	944	0.192
15.4	1000	0.841
21.0	....	1.75
26.2	....	2.45

That the bombardment by the cathode particles did not reach a maximum at the highest of the vacua attained in our experiments is clearly indicated in the curve for the synthetic ruby (fig. 116). The intensity of luminescence of this crystal increased in direct proportion to the tube-voltage above 10 kv., at which point the cathode stream appears to have reached its maximum and constant value.

In view of the fact that these oxides are also capable of flame excitation, one of the most obvious explanations of their luminescence in the vacuum-tube would be that the bombardment dislodges portions of the oxide and that it is either the return of these displaced particles that produces fluorescence or that the material thus partly reduced combines, giving luminescent effects with free oxygen from the tube. As against the second supposition we found that the rejuvenation of the glow occurred about equally well, whether air, pure oxygen, or hydrogen was introduced, or whether the pressure change was produced by heating the nichrome strip and driving off its occluded gases, or finally by reducing the pressure by the use of liquid air, instead of pumping, and increasing it by the release of the frozen vapors. In this last case especially there would seem to be no change in the free-oxygen content of the tube, but only change of pressure.

The inference would be that the fluorescence is produced by recombination with oxygen slightly displaced rather than with free oxygen. That the effect is not due to heating by the cathode particles was very clearly brought out when the heating strip was coated with calcium oxide. The passage of an electric current through the strip enabled us to change the color of the glow of this coating from a ruddy yellow to green before a visible red heat was attained. Cathode bombardment did not, however, appreciably change the color of the strip, and since the intensity changes with pressure went on at any temperature of the coating, within the temperature range of its activity, it was certain that we had to do with a pressure change rather than a temperature change. In what way the gas-pressure affects the actions and reactions, electronic or chemical, upon which the luminescence of these oxides depends, remains thus far merely a matter of surmise. It might be suggested, however, as a matter not as yet actually established, that the more intense cathodic bombardments in the higher vacua tend to drive the oxygen completely off, so that there is less and less of the recombination which produces fluorescence. Hence the diminished intensity at higher vacua.

That this effect is not common to cathodo-luminescence in general we know from the work of Veazey and T. B. Brown,[1] from Lenard's[2] earlier experiments, and from our measurements on the ruby, just

[1] T. B. Brown. Physical Review (2), 11, 1918, p. 39–57.
[2] Lenard. Annalen der Physik, 12, 1903, p. 449–490.

described. It is, indeed, doubtless an effect peculiar to these oxide films and perhaps incident to their mode of preparation.

The case of aluminum oxide in this respect is instructive. This oxide, as has been known since the extended researches of Crookes, Urbain, LeCoq de Boisbaudran, and others, exhibits a great variety of colors in the vacuum-tube—green, red, and blue and the combinations of these. It is a question of impurities and of heat treatment—a matter to be discussed in a subsequent chapter. The combination of red and blue occurs frequently, giving rose-colors and purples.

We find that when such a specimen is subjected to cathodic bombardment the blue appears first, at the higher pressures, and is gradually replaced by red as the vacuum is improved, so that we have successively in the same specimen a high-pressure glow (blue) and a high-vacuum glow (red).

The immediate tentative explanation, as above, is that the oxygen is more or less loosely attached as the result of different previous heat treatments, etc., so that the pressure relations of the two bands of the fluorescence spectrum are altogether different.

EXPERIMENTS WITH TITANIUM OXIDE

Although the films of TiO_2 prepared by the method of sublimation were found to be inactive, a sample of unusual purity which became available later[1] gave the following interesting result in the cathode-tube:

When this sample of TiO_2 was placed in a vacuum-tube without previous heat treatment, the only sign of activity was a very faint ruddy fluorescence under bombardment by the cathode-rays. This glow, when viewed with a hand spectroscope, shows indications of a group of narrow bands in the orange-red, but these have not as yet been measured on account of their weakness.

When, however, the surface layer of the oxide had been fused in an alundum crucible with the oxyhydrogen flame impinging upon it from above, the glazed crust formed upon cooling gave a fine *blue fluorescence,* the spectrum of which appeared to consist of three broad overlapping bands with crests at, approximately, 0.625μ, 0.550μ, and 0.475μ (visible to 0.450μ). The intervening regions in the yellow and green-blue were noticeably dim. Upon standing in the air the fused oxide lost in great measure its power of cathodo-luminescence. Indeed, its fatigue within the vacuum-tube during bombardment was unusually rapid. Freshly fused samples, during the earlier stages of evacuation, glowed more brightly than at any subsequent time. In its behavior this substance corresponds very closely with the oxides of calcium, silicon, and zirconium.

[1] To the courtesy of Mr. W. L. Lemcke, the writer is indebteded for an ample supply of this oxide, which had been prepared by Dr. Rossi.

The flame excitation of this sample of TiO_2 has already been recorded; the character of its radiation when incandescent will be considered in Chapter X.

III. THE PHOSPHORESCENT SULPHIDES

These substances differ from the oxides just considered in that they are strongly photo-luminescent at ordinary temperatures, owing to the artificial or sometimes accidental admixture of some active element, such as bismuth, copper, lead, or antimony.

The solid solvent of those which respond to the flame is usually calcium sulphide; sometimes strontium sulphide; never, so far as at present known, barium sulphide. Zinc sulphide in the form of Sidot blende is also highly sensitive to flame excitation.

A phosphorescent sulphide differs from the oxides already described in that at room temperature it usually reacts to the ultra-violet radiation from the hydrogen flame even at a considerable distance. When warmed by the radiation, even though not in contact with the flame, it shows thermo-luminescence. Then, having become dead to all photo-excitation, it will still respond to flame excitation if brought into the active zone and heated there to the proper temperature.

That the flame excitation of these sulphides is not due to a conversion of the surface layer into the oxide is indicated by the color of the luminescence, which corresponds to the cathodo- or photo-luminescence of the sulphide and not to the flame effect as observed in the oxide.

Spectrophotometric measurements, moreover, have been made by one of the present writers (Howes). These were extended to three Lenard and Klatt sulphides, the spectra of which have been described in a previous chapter, and it was found that the spectra of these, under flame excitation, were composites of *the same groups of narrow components* which make up their spectra in the case of photo- or cathodo-luminescence. (See further, Chapter XII.)

The response of these substances to light after cooling indicated that no permanent decomposition occurred under the action of the flame. At higher temperatures, as in the electric arc, the sulphides were, however, converted into the corresponding oxide and the flame luminescence became that characteristic of the oxide.

While a so-called active element in solid solution is generally conceded to be necessary to the production of a phosphorescent sulphide, this does not seem to be essential in flame excitation. What was found for the oxide in this respect applied to the sulphides also. A sample of zinc sulphide which was so pure as to be quite inert under the iron spark, both as regards fluorescence and phosphorescence, responded brilliantly with a yellow-green glow in the hydrogen flame

at a red heat. The effect became distinctly visible at 560° and was strong at 616°, much brighter indeed than the luminescence under like conditions of specimens of Sidot blende especially prepared with a view to phosphorescent properties. This same pure zinc sulphide responded strongly under cathode rays at room temperature, but was without persistent after-glow.

Attempts to determine the upper limit of the luminescence were less definitely successful. Above 900° the glow was feeble but discernible, and at 934° the highest temperature attained in this run, it had not altogether vanished. We were now almost at the upper limit for ZnO as described in a previous paragraph, and it seemed almost certain that portions of the sulphide had been converted into the oxide.

Calcium sulphide, when pure, is inert alike under photo-excitation and cathode bombardment. A sample which fulfilled these criteria of freedom from admixtures was found, however, to be excited by the hydrogen flame through an unusually wide range of temperatures. When placed in a very thin layer on the surface of the copper block and gently heated it showed flame luminescence quite definitely when the block was heated to 60° C. The color was *bluish-green.* The intensity increased in brightness with rise of temperature, and below the red heat there was a rather sudden change to a much brighter yellow glow—a lemon yellow and very luminous. This continued with growing and then waning intensity until a cherry-red heat of the block was reached, when it vanished. Measurements of the highest temperature at which the luminescence could just be perceived were made with the Pt-Cu thermo-junction, and nearly simultaneously with the Morse thermo-gage, with the following result:

Vanishing temperature by pyrometer	744° C.
Vanishing temperature by thermo-junction	735° C.

An attempt to pick up this temperature again as the block slowly cooled gave

Pyrometer	731° C.
Thermo-junction	730° C.

Taking the average of these four estimates, we have 737° C. as the temperature of the surface of the block and the approximate temperature of the coating. The yellow glow increased rapidly as the block cooled further and was apparently at its brightest somewhat below 500°. The transformation to the blue-green occurred at 330° according to the indications of the thermo-junction. At this temperature the very thinnest parts of the coating which were nearest the metal and therefore cooler had changed while the high points were still at a bright yellow.

Calcium sulphide may therefore be added to the list of those substances having two stages of flame luminescence. The temperature ranges were as follows:

Lower stage	60° to 330° C. (blue-green)
Upper stage	330° to 737° C. (bright yellow)

IV. CALCITE, FLUORITE, AND OTHER CRYSTALS

Of the crystals thus far tested for flame luminescence, calcite and fluorite especially merit detailed mention.

A crystal of calcite in the flame is at first inactive. Then its edges begin to glow brightly, framing the otherwise dark crystal in lines of light, and the light very gradually extends over the faces. Examination shows that decomposition of the carbonate precedes luminescence. This occurs first along the exposed edges and later over the faces of the crystal. The glow seems to depend on the presence of this film of oxide.

The obviously localized and superficial glow produced by flame excitation is altogether different from the phenomenon of thermo-luminescence, as produced by the same flame, when applied to certain calcites or to kunzite or fluorite. In thermo-luminescence the effect is seen to pervade the entire body of those portions of the crystal which have attained the requisite temperature; in flame excitation proper it is confined to those portions of the *surface* which are within the active zone of the flame.

Several specimens of fluorite were examined. Of these, some showed the characteristic blue-violet fluorescence under the action of the iron spark. Others, which were mostly of a yellowish body-color, did not respond visibly to photo-excitation. All, however, were more or less thermo-luminescent, and all showed the same *pale greenish-white* flame luminescence.

The temperature limits observed in the case of one of the almost white, clear, transparent crystals were as follows:

Lower limit	58° C.
Upper limit	310° C.

Upon heating to a much higher temperature, this crystal began to be converted into the oxide along its edges. Upon cooling it developed a very bright fluorescence under excitation of the flame, having the yellow color characteristic of calcium oxide, which was picked up at about the usual temperature, *i. e.*, 690°.

The significant feature in the behavior of these fluorites is that while they differ in color and in their response to photo-excitation—differences usually ascribed to the presence or absence of admixtures of the rare earths, etc.—they are all much alike, if not identical, under flame excitation, from which, as in various previous experiments, we

infer that flame excitation does not depend on foreign admixtures.

A similar result is obtained in the case of aluminum oxide when crystallized either as synthetic ruby or white synthetic sapphire, or as native sapphire from North Carolina, or as corundum. All of these crystals showed the same *pale-green* fluorescence as the powdered oxide described in the paragraph on the active oxides. *These crystallized forms,* however, all gave the red fluorescence of the ruby when tested in the cathode-tube, because presumably of the presence in all of traces of chromium.

How general an effect flame luminescence is among crystals and also among compounds other than the oxides and sulphides remains to be determined. As has already been indicated in the list of substances thus far found active, boric acid and telluric acid respond to the flame. Crystals of the latter compound, even during the process of being decomposed by the flame, glow with a vivid green light.

From our present evidence it appears probable that only those materials will become luminescent under the action of the hydrogen flame which are capable of the proper sort of rapid reduction and subsequent oxidation already described and that the active range of temperatures in each case is that within which the above reaction occurs.

SUMMARY AND CONCLUSIONS

(1) Flame excitation occurs when certain substances are brought into the zone of a hydrogen flame between the regions of reduction and oxidation.

(2) It occurs, so far as known, in certain oxides and sulphides, in a few phosphorescent preparations, and in certain crystals and inorganic salts.

(3) Many substances, such as calcium tungstate, willemite, and many of the Lenard and Klatt sulphides, which are strongly luminescent under the action of the usual modes of excitation, do not respond to flame excitation.

(4) The effect does not appear to depend on the presence of traces of activating elements. Such admixtures may modify the character of the fluorescence; they often inhibit it altogether. Thus, pure cadmium phosphate responds to flame excitation, but the addition of manganese, which renders it strongly photo-luminescent with a well-known red phosphorescence destroys its susceptibility to excitation by the flame.

(5) The spectra obtained by flame excitation are characteristic fluorescence spectra consisting of two or more overlapping bands. Each band is made of numerous components forming sets of equal frequency-intervals, and these components in all the cases thus far

investigated are identical with the components of the fluorescence spectrum of the substance when photo-excited.

(6) Flame excitation occurs through a definite range of temperatures. The temperature limits thus far studied are shown in table LVII.

TABLE LVII—*Colors and temperature limits of flame excitation*

Substance	Lower limit	Upper limit	Color of band	Substance	Lower limit	Upper limit	Color of band
	°C.	°C.			°C.	°C.	
SiO_2.....	85	367	White	ZrO_2.....	76	372	Blue-green
					440	720	Red
MgO.....	75	680	Blue-green	ZnO.....	568	704	Red
					704	948	Green
Al_2O_3.....	55	692	Pale green	ZnS.....	0±	123	Yellow
					211	575	Blue-green
CaO.....	0±	600	Red	CaS.....	60	330	Blue-green
	40	725	Green				
	0±	425	Blue-gray	CaF_2.....	58	310	Yellow-green
TiO_2.....	425	677	Red				
	677	1000	Yellow	$Cd_3(PO_4)_2$....	50	733	Yellow

These values are to be regarded as only approximate. The fluorescence in all cases is doubtless complex, there being at least two broad bands. These bands have their own independent ranges of temperature and the effect observed is usually a composite. In the case of CaO, the two temperature ranges greatly overlap. In that of ZnO they barely overlap. The bands of ZrO_2 and ZnS are quite distinct as to temperature. The phenomenon with the sulphides is complicated by the probability of a change into oxides at the higher temperatures. Both CaS and ZnS exhibit bands above the temperatures of the table which coincide as to color and upper limit with those of the corresponding oxide. These have not been included.

(7) Excitation of these substances to fluorescence does not occur by heating in air or hydrogen, nor in vacuo, nor by contact with a jet of hydrogen while hot unless the hydrogen be ignited and conditions are favorable for free oxidation.

(8) Luminescence does, however, occur by cathode bombardment throughout essentially the range of temperatures indicated under heading (6), but the effect is not identical, since the bands are not excited in the same proportions as in the flame. X-rays also excite many of the substances in question at high temperatures.

(9) The after-glow, in so far as the same has been studied, follows the law of vanishing phosphorescence.

(10) The action of strong static fields having been found without effect, also the use of powerful photo-excitation at high temperatures and the substitution of other flames for hydrogen, the explanation

put forth in an early paragraph is tentatively adopted, *i. e.*, that flame excitation is a dual process in which reduction and oxidation rapidly succeed each other in an unstable layer within the flame between the region where reduction is continuous on one side and oxidation on the other. The alternative suggestion that it is due to disturbances arising from the formation of H_1 or H_3 and their subsequent recombination to H_2 is not positively excluded. The work of Bonhoeffer[1] on luminescence produced by active hydrogen indicates that H_1 may take part in the mechanism, which, however may still be a fluctuating one.

[1] Z. Bonhoeffer. Physik. Chem., 116, 391-400, 1925.

CHAPTER IX

PHOTO-LUMINESCENCE OF FLAMES[1]

Luminescence is, at the present time, commonly regarded as a phenomenon of instability, occurring chiefly, if not exclusively, where matter is dissociating and is entering into new combinations. The conditions within a flame are therefore peculiarly favorable to the production of luminescence, and the light from flames containing salts, etc., is quite generally ascribed by the chemists to "flame reactions rather than to the direct effect of temperature."[2] Whether the materials within a flame, being in a state of rapid dissociation and recombination, are capable of excitation to luminescence by extraneous means appears never to have been considered.

The present writers were led to look for photo-luminescence in flames by discrepancies in some attempted measurements of the opacity of a hydrogen flame rendered luminous by the injection of powdered calcium fluoride. The brightness of the flame plus the light transmitted by the flame from a nitrogen-filled tungsten lamp placed behind it should normally be slightly less than the sum of the two intensities taken separately, whereas instead of showing a loss by absorption, the *combined brightness was persistently greater.* Various more obvious explanations having been disposed of, we were driven to the conclusion that the flame was actually somewhat brighter when exposed to the light of the neighboring source.

The experiments which followed this entirely unanticipated result are described below.

THE METHOD

In the observation of the flames under consideration, all of which had bright banded spectra of the familiar type obtained when salts of Li, Na, etc., are introduced into a nonluminous flame, it was advantageous and convenient to deal with a single band instead of with the flame as a whole. For this purpose a Hilger constant-deviation spectrophotometer was used, the collimator slits of which were maintained at constant width. As in various investigations already described, intensities of the contrast field were balanced by moving the comparison light *T,* figure 117, a small nitrogen-filled

[1] Nichols and Howes. Phys. Rev. (2), XXII, 425-431, 1923; XXIII, 472–477, 1924.

[2] For a very complete discussion see Bancroft and Weiser, J. Phys. Chem., XVIII, pp. 8, 213, 281, 762; XIX, pp. 310, 1915.

tungsten lamp maintained on a storage-battery circuit, along a photometer bar in front of the slit C_2. The flame F was directly before the other slit C_1.

The flame in most of our experiments was a hydrogen flame from an ordinary blast-lamp. The salt which rendered it luminous was introduced with the air-supply either in the form of a dry powder or of spray. In the former case the blast of air entered a short glass tube T, figure 118, A, through a narrow vent bent downward so as to stir up the surrounding powder and carry a portion into the flame.

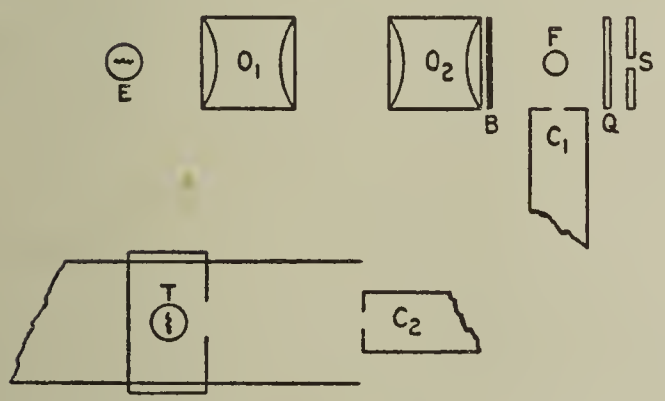


FIG. 117—Diagram showing arrangement of apparatus

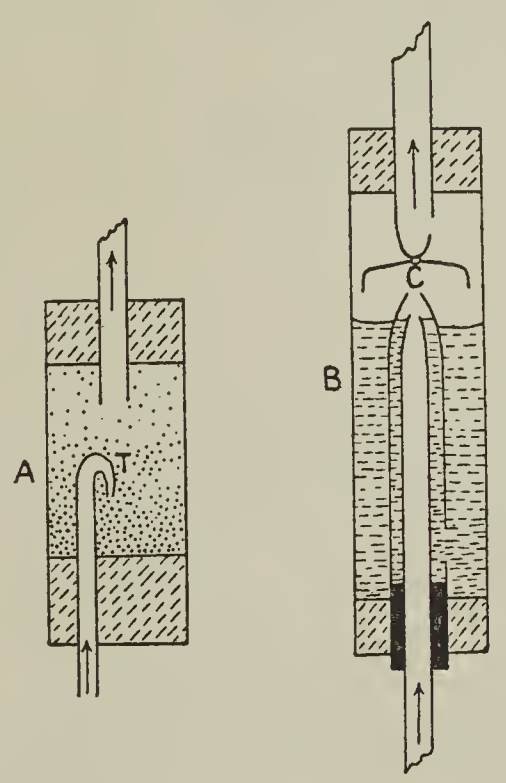


FIG. 118—Devices for introducing salts into flame; A, in powder form; B, in solution

This method afforded a very bright flame when dry powders were obtainable, $CaFl_2$, SrS, NaCl, etc., but the steadiness was inferior to that of flames supplied with a sprayed solution. In later measurements, therefore, the aspirator described by Bancroft and Weiser[1] was used. It consisted of an Argand chimney, B, figure 118, closed at both ends, with the usual double tube having contracted tips inserted through the base. The outlet above was shielded by a suspended crucible cover, C.

Having established the fact that the increase in brightness of the hydrogen flame was practically independent of the direction from which it was illuminated, which was quite what one would expect in the case of luminescence, we mounted a pair of lantern objectives of large aperture, O_1 and O_2, figure 117, with their common axis at right angles to that of the collimator. The exciting source E was placed at the principal focus of O_1 and its image fell within or sometimes just beyond the flame, so that the pencil of rays passed through that part of

[1] J. Phys. Chem., XIX, 311, 1915.

the flame which was in line with the collimator. A swinging shutter, *B*, which could be moved by the observer at the eye-piece of the spectrophotometer, served to admit or exclude the exciting light.

While it is a simple matter to detect with certainty variations of the order of 5 per cent due to light added to or subtracted from an otherwise steady source of light, to do so in case of a rapidly and irregularly fluctuating flame is not a matter of mere inspection. The increment due to exposure is immediately submerged in the natural

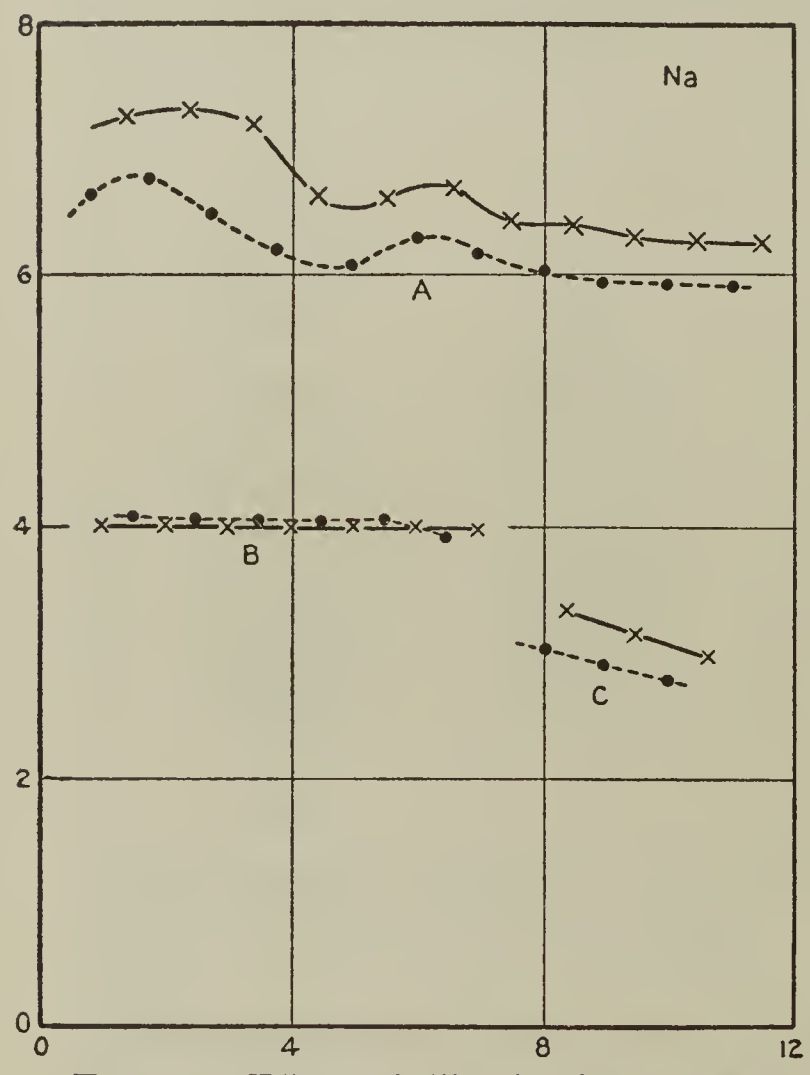


FIG. 119—Effect of illumination on a sodium flame

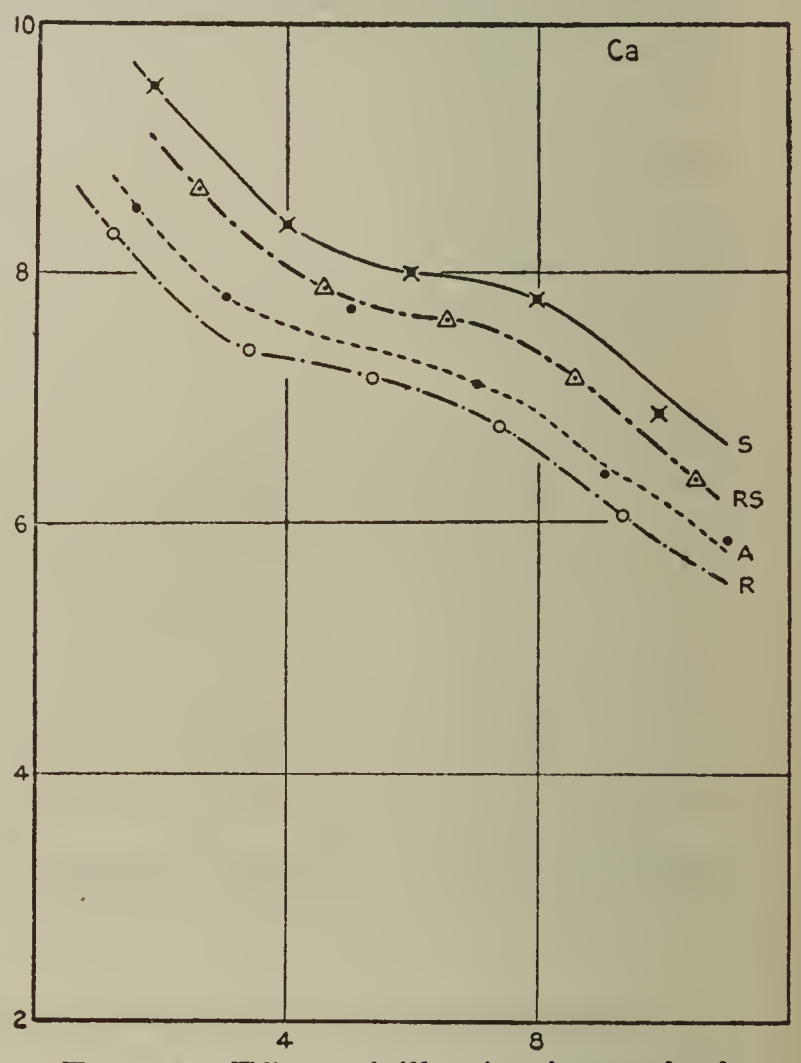


FIG. 120—Effect of illumination and of quenching on a calcium flame

drift, and the only satisfactory method is to make a considerable number of settings rapidly, and at nearly regular intervals of, say, thirty seconds with the flame alternately exposed and unexposed. Two observers, of whom one opens and closes the shutter and reads the photometer bar while the other sets the comparison lamp promptly upon signal, never readjusting his setting and ignoring so far as possible the position of the shutter, can obtain very consistent results in this way. If the readings thus made are plotted as though the time intervals were constant, which strictly speaking they are not, an immediate indication is had of the character and approximate size of the effect. Numerical values may then be obtained by averaging over the ranges within which disturbances are least troublesome. Effects too small to be detected by the observer at the eye-piece, because of the drift, are thus brought out with certainty. Figures 119 and 120 will serve to elucidate this procedure.

THE RESULTS

Of the various exciting sources employed, including the tungsten lamp, the carbon arc, the mercury arc, and an iron spark, the spark was relatively the most effective. From this it was clear that the *enhancement of the bright bands of these flame spectra is produced by radiation of the shorter wave-lengths.* Moreover, since the effect was greatly reduced (*e. g.,* from 5.9 to 3.6 per cent in an experiment with the lithium flame) by inserting a glass plate instead of quartz between the spark and flame, there was obviously considerable excitation by wave-lengths for which glass is opaque. On the other hand, we obtained marked excitation through a deep-purple glass which, aside from the usual cobalt band in the red, was opaque to all wave-lengths up to 0.43μ. The near ultra-violet was thus indicated as an active region.

Measurements with various light filters interposed between the flame and the exciting source, a tungsten filament, revealed further the existence of a *quenching effect of the longer wave-lengths* of the visible spectrum analogous to the action of infra-red rays upon the phosphorescent sulphides. A sodium flame upon which the image of the glowing filament was focussed was increased in brightness by exposure as shown in figure 119, *A,* in which readings with and without excitation were made alternately. The average effect for this run was + 6.0 per cent. A repetition with a deep-amber glass interposed gave the result shown in figure 119, *B,* where the effect of illumination, although very slight, was distinctively negative (—1.2 per cent). Upon removing the screen (fig. 119, *C*) the conditions indicated in figure 119, *A,* recurred.

Quenching is still better exhibited by an experiment in which the hydrogen flame was supplied with spray containing $CaCl_2$. Excitation was by an iron spark, *S,* figure 117, placed about 5 cm. from the flame, with a quartz window interposed. The flame could likewise be exposed at will to a red light from the tungsten filament by means of a dense ruby glass placed between the lenses O_1 and O_2, figure 117.

Calcium band at λ 0.6475μ—Observations were made upon the red band of the calcium flame at 0.6475μ, a wave-length which was *included within the band transmitted by the ruby glass.* This was a coincidence favorable to test the analogy to the quenching of the phosphorescence of the sulphides, since, as is well known, the only active rays in that case are those corresponding in wave-length to an absorption band of the substance.

The procedure in the present experiment was to measure successively the brightness of the band with the flame (1) unexposed, (2) exposed to red, (3) excited by the spark, (4) excited by the spark and also exposed to red. This cycle was repeated several times with

results which are indicated graphically in figure 120, where curves *A, R, S,* and *RS* give the brightness of the band in the four successive steps, respectively.

From these curves it will be seen that enhancement by illumination (compare curves *A* and *S*) is about 11 per cent; the quenching effect (compare curves *A* and *R*) is likewise unmistakable, and equal to about 2 per cent; and the combined effect of the spark and the red light is an enhancement of about 5 per cent.

From this it appears that while the red light reduces the brightness of the observed band in the spectrum of the unexposed flame by only 2 per cent, it cuts down the effect of the spark upon the flame to one-half of its normal value. In other words, *the quenching by red light affects chiefly, perhaps wholly, the photo-excited luminescence of the flame.*

To explain the effect of the red light upon the unexposed flame, we may suppose that although visible radiation, in so far as it is due to mechanisms other than those put into motion by the exciting light, is not subject to quenching, a certain amount of auto-excitation exists, the materials capable of photo-luminescence being affected by the violet and ultra-violet radiation within the flame itself.

Strontium band λ 0.655μ—Measurements similar to those just described were made upon the red band λ 0.655μ of a strontium flame, *i. e.,* of a hydrogen flame supplied with a spray of $SrCl_2$. The average results for the increase of brightness are: (1) effect of spark excitation, +9.7 per cent; (2) effect of exposure to red, —2.6 per cent; combined effect of spark and red, + 5.7 per cent.

Lithium line λ 0.6708μ—In some observations upon the red line, λ 0.6708μ, of a lithium flame, advantage was taken of the fact that the transmission band for red of a sheet of cobalt glass included the wave-length of the lithium line. The exciting light from a tungsten filament was passed through this glass before being focussed upon the flame. The red light from the exciting source could be cut out by interposing as a second filter a cell containing a suitable solution of ammonio-sulphate of copper. Readings upon the brightness of the lithium line made alternately through the cobalt glass alone and through both filters, showed increased intensities when the red light was removed. Without correcting for the diminished strength of excitation due to absorption by the second filter, this increment exceeded 30 per cent of the total photo-luminescence. Similarly, it was found that the exciting power of a source, such as the carbon arc, was measurably increased by the interposition of a screen opaque to the longer wave-lengths of the visible spectrum.

Sodium lines—Experiments on quenching of the sodium flame with red light gave a negative result, the average intensity of the yellow

lines being the same, when exposed as when unexposed, to within 0.2 per cent, or in other words, to well within the errors of setting. When however, an amber glass screen was used as described in our earlier paragraph instead of the ruby glass, quenching occurred to an extent easily measurable. In the former case there was presumably but little absorption by the luminescent material; in the latter there would be complete absorption in the region of the lines of sodium at 6,154 and 6,160.

Effects similar to those obtained by the use of light-filters in the foregoing experiments were likewise produced by focussing the spectrum of a linear filament in the vertical plane through the extension of the axis of the collimator *C* and exposing the flame under investigation to different portions of the spectrum.

In these tests, in which Mr. T. Tanaka, a practiced experimenter with the spectrophotometer, kindly acted as observer at the eyepiece, excitation was obtained with the shorter wave-lengths, and this was changed to quenching when the flame was exposed to red. The results with these necessarily feebler illuminations were not of a size to warrant an attempt to work out the effect, wave-length by wave-length, with monochromatic light.

Relative effects on different bands of the same spectrum—Thus far effects on a single band only have been described. Measurements of several of the brighter bands in the flame spectrum of calcium and strontium indicated, however, that under a given excitation there was enhancement of all the bands in approximately the same proportion, whether the band was in the red, orange, or green. Under the action of the inhibiting rays, it was found likewise that quenching was not confined to the band lying within the region of the light transmitted by the filter, *but was equally apparent in bands lying beyond that zone.* It is therefore concluded that the emission spectrum of a flame is to be regarded as a unit. *When it is excited to luminescence all its bands are enhanced, and when it is exposed to quenching by absorbed light all its bands are quenched.*

Variations in flame sensitiveness—Early in the course of these experiments it was noticed that the sensitiveness of flames to photo-excitation differed greatly. The flame of the Bunsen burner, for example, was found to be almost entirely unaffected. The upper portion of the hydrogen flame with admixture of air, as used by us, was more sensitive than the base. A set of measurements on the sodium flame to determine this difference gave for a region near the tip 7.4 per cent and for one near the base 5.5 per cent, the exciting source being the same for both cases.

Fluctuations in sensitiveness produced by slight adjustments of the air-blast suggested a dependence upon the supply of free oxygen,

and this was tested by enriching the surrounding atmosphere with this gas. In this way a rather insensitive calcium flame was increased in sensitiveness from 4.3 per cent to 9.1 per cent for a given illumination.

Relation of photo-luminescence to flame contents and flame reaction—In the class of flames upon which the observations thus far described were made, certain chemical constituents are present and certain flame reactions occur. For a hydrogen flame into which calcium chloride has been introduced, for example, we shall have, among other substances, Ca and Cl (in both atomic and ionized form); also CaO. In such a flame there must be continually going on the dissociations and recombinations commonly accompanying the phenomenon of luminescence. Since no new bands are introduced by photo-excitation, it seems reasonable to suppose that the vibrating mechanisms which produce the flame spectrum are the ones excited to additional activity by light.

EXPERIMENTS WITH A MODIFIED FORM OF FLAME[1]

Our study of flames led ultimately to the adoption of the form shown in figure 121, in which *A* is an ordinary acetylene burner (of steatite), supplied from a tank of compressed hydrogen. Air containing finely divided spray from a solution of the salt to be used was carried from the aspirator (not shown) to the immediate proximity of the air-ducts of the burner through the tubes *T*, *T*, whence it was drawn into the flame. A further supply of impregnated air from the same aspirator was delivered to the outer face of the flat flame *F*, through narrow longitudinal slots in two tubes, *L*, *L*, mounted horizontally and parallel to the faces of the flame near its base. In this way the salt is conveyed simultaneously to the body and to the surface layers of the flame, with better results than when the spray is introduced into the hydrogen gas before the latter enters the burner.

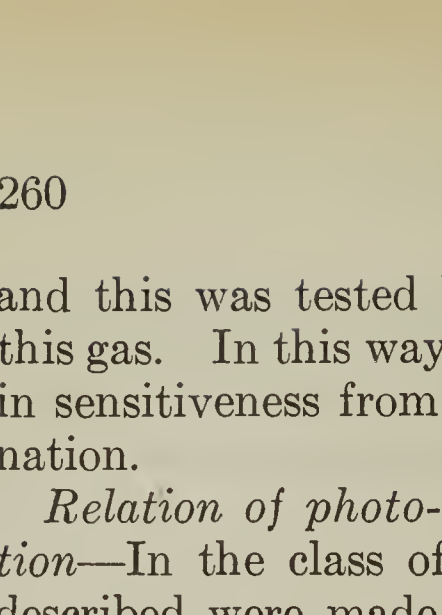


FIG. 121—Form of flame adopted

CHANGES IN THE FLAME SPECTRA

The source of excitation selected for use in most of the experiments to follow was an "amalgam arc" in quartz. This source of radiation has the following good qualities: It is weak in the quenching rays of the red, rich in the violet and ultra-violet, and reasonably steady.

[1] Nichols and Howes. Phys. Rev. (2), XXIII, p. 472–477, 1924.

When one of the flames under consideration is excited by such an arc or by any source capable of producing luminescence, and is studied by means of a spectrophotometer, as in our earlier experiments, an observer at the eye-piece is aware of certain rather obscure changes in the appearance of the spectrum.

The increase in brightness may not be immediately obvious; changes of intensity, indeed, can best be studied by removing the eye-piece and balancing the contrast field of the instrument. With sodium or lithium in the flame there is of course little else to observe, at least with the dispersion afforded by a single prism. One is, however, aware of a change when the shutter between the arc and the flame is opened. The line-like band becomes sharper as to its edges

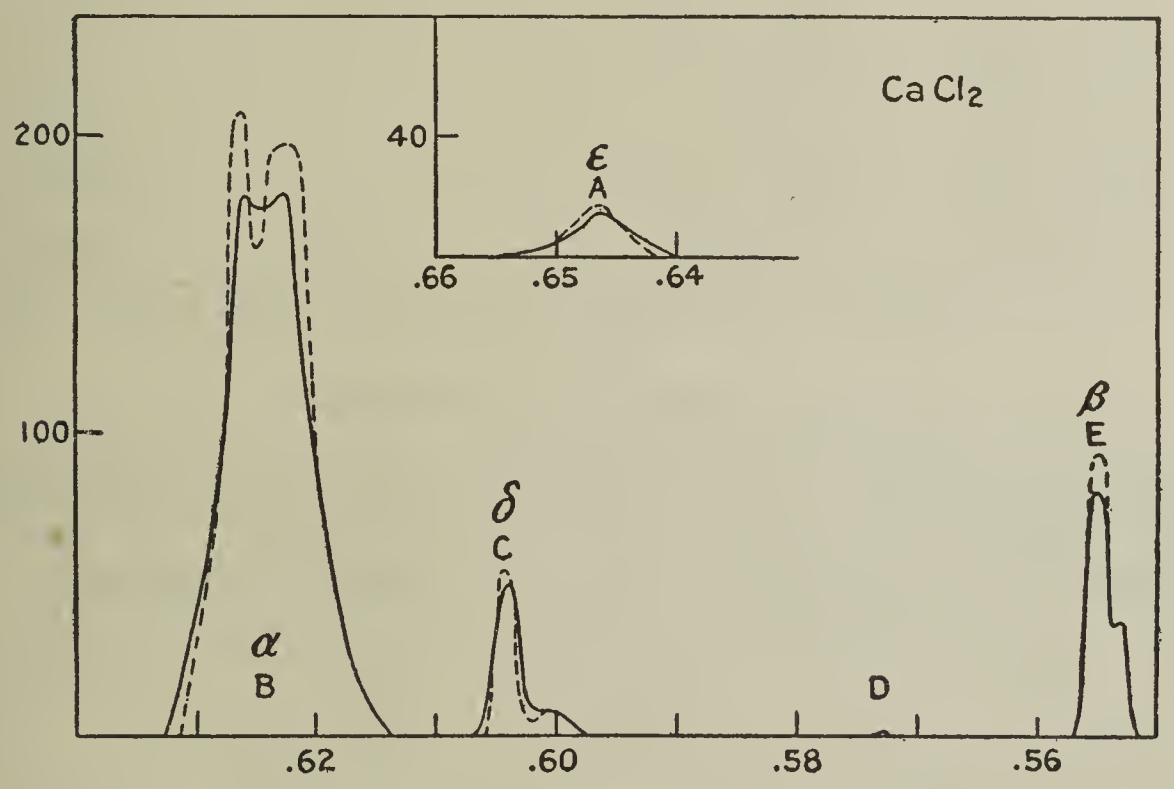


FIG. 122—Spectrum of calcium flame

and the dim background, however free from stray light, becomes blacker when the flame is illuminated.

It seems probable that we have to do with changes in the structure of the band, similar to those described by Strutt[1] in his experiments upon sodium vapor in vacuo, but these were quite beyond the power of the constant-deviation instrument at our command.

The broader bands in the spectra of calcium, strontium, and barium afford an easier field. Appreciable shifts of the edges occur on excitation and various structural changes may be perceived. Observations of these effects were made throughout the visible spectrum, and the results are indicated in figures 122, 123, and 124. In these diagrams the bands are lettered *A, B, C,* etc., beginning at the red end of the spectrum, and the customary designations α, β, γ, etc., as used in spectrum analysis, are added. The various bands are

[1] R. J. Strutt. Proc. Royal Soc., XCVI, p. 272, 1920-21.

drawn in solid lines and the changes brought about by exposure to the exciting light are shown by broken lines.

Measurements upon which to base these sketches were made as follows: (1) Edges, crests, and the depressions between crests, when

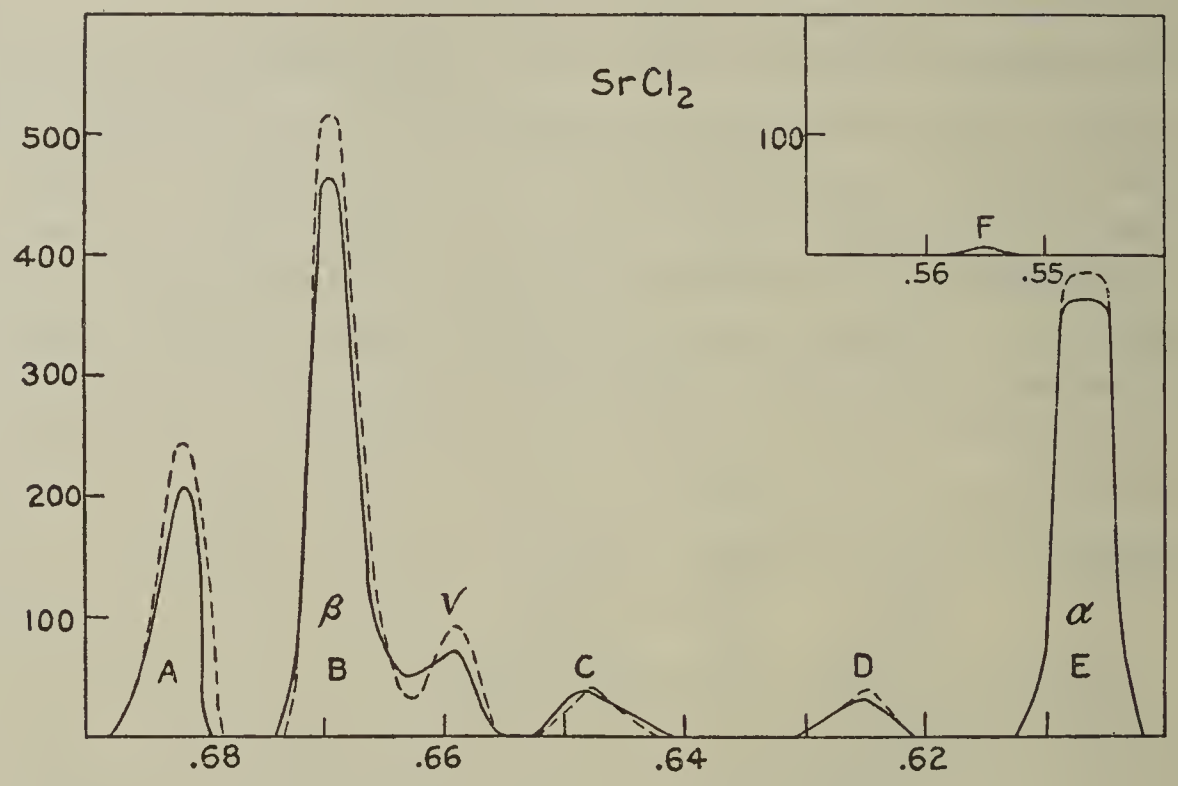


FIG. 123—Spectrum of strontium flame

such were perceptible, were located before and during excitation; (2) the brightness of each crest and the amount of light in the depressions were estimated before and during excitation.

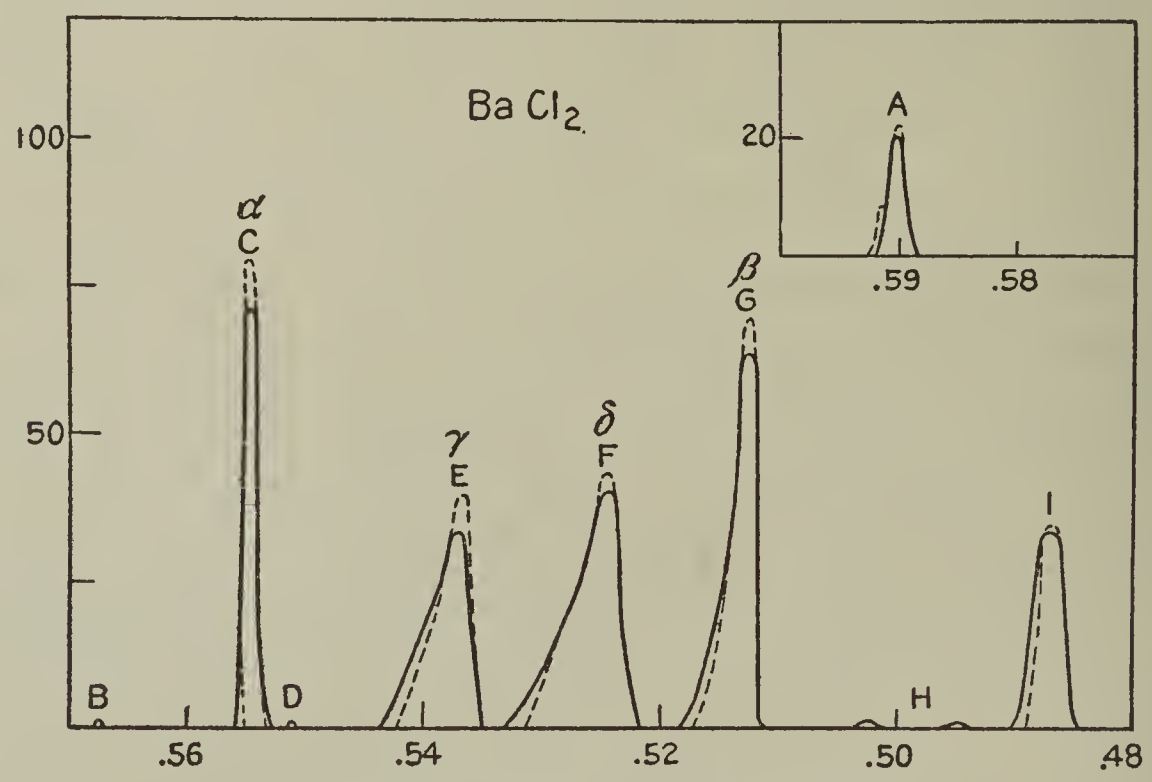


FIG. 124—Spectrum of barium flame

It will be seen from the figures that the movement of the edge of a band upon excitation is nearly always inward, so as to produce an effect of narrowing, and that the change occurs chiefly at the tail of the band rather than on the steeper slope (see particularly in this

regard the three bands *E, F, G,* in the spectrum of barium (fig. 124), all of which tail off in a similar manner toward the red). The unsymmetrical narrowing gives the impression of a shift of the band, but it will be noted that the crests are not shifted perceptibly by excitation. They are increased in intensity, however, and the depressions between crests (see bands *B* and *C* in fig. 122 and *B* in fig. 123) are deepened, but also without shift.

This deepening of the depressions is one of the striking effects of excitation. The existence of a depression in a broad-crested band and of the accompanying resolution of the band into the two components of which it consists sometimes becomes evident only when the flame is exposed to the exciting light.

All crests are enhanced during excitation, and in nearly equal proportions. Comparison of bands where observations were not simultaneous are of doubtful value in this respect because of the fluctuating sensitiveness of these flames, but to watch the sudden outcropping of the left-hand crest of band *B* or of band *E* in the spectrum when a calcium flame is exposed to light is to be convinced of the selective character of the effect.

REGIONS OF PHOTO-LUMINESCENT SENSITIVENESS

In one of the foregoing paragraphs the statement was made that the photo-luminescence depended upon the conditions of combustion. In these later experiments, in which an image of the flame was focussed sharply upon the slit of the spectrophotometer, and in which we were able to explore the flame laterally, a more specific result was obtained. It was then found that the sensitiveness to excitation was chiefly confined to certain narrow layers of the flame, and particularly to the boundary between the oxidizing and reducing regions. In other words, the sheath surrounding the main body of the flame, which is most active in producing luminescence when brought in contact with various oxides (see Chapter VIII), is also the chief seat of the photo-luminescence of the flame itself. Turbulence, which tends to destroy the integrity of this boundary, is therefore detrimental to the effect, whereas certain quietly burning flames have been found peculiarly sensitive.

THE THALLIUM FLAME

A flame impregnated with spray containing thallium chloride and exposed in the usual way to the light of the amalgam arc showed an extraordinary and unlooked for activity. When the shutter was open the green line of thallium was increased in intensity over 50 per cent and in some subsequent trials *over 50 times,* an effect which was striking, whether viewed directly through the eye-piece of the spectrophotometer or indirectly by use of the contrast field of the Lummer-Brodhun prism.

The very great activity of this particular flame was finally traced to the unsuspected existence of thallium in the mercury of the arc lamp and to the consequent presence of the powerful lines of that element at 5,350.7, 3,775.9, and 3,519.4 Å. Although owing to the small amount of thallium in the amalgam these lines did not compare in brightness with the neighboring lines of mercury, they were easily visible, the green line directly and the ultra-violet lines by the aid of a fluorescent screen. Interposition of a plate-glass screen 1 cm. in thickness did not diminish the excitation appreciably, hence it was inferred that the effect was not due to the action of the far ultra-violet. A glass transmitting the violet and near ultra-violet, but opaque to the green line, gave a somewhat reduced excitation, while a filter opaque to all beyond the green weakened the effect still more. From these observations it seemed that the lines at 5,350, 3,776, and 3,519 were jointly responsible for the photo-luminescence of the flame.

To put this conclusion upon a still more definite basis, the slit was removed from a large Hilger quartz spectrograph and the contracted portion of the quartz tube of the amalgam arc, which has a diameter of about 3 mm., was mounted in its place. In this way any desired portion of the visible or ultra-violet spectrum could be focused within the hydrogen-thallium flame. The principal lines of the amalgam arc were sufficiently separated in this spectrum to permit of their use individually for excitation.

Although the effects obtained by this method were much smaller than when the undispersed light of the arc was used, the results were perfectly definite and decisive. It was found that while the intense mercury lines at 4,359 and 3,126 produced *no excitation whatever* (the average sets of readings of the intensity of the thallium line 5350 with and without exposure being identical), the region containing the thallium lines 3,776 and 3,519 enhanced the green line by about 7 per cent, two sets of readings giving respectively 7.6 and 6.8 per cent. The line at 3,776, taken alone, the adjoining mercury line at 3,650 and the thallium line at 3,519 being excluded, gave 3.1 per cent excitation. The region of the visible spectrum containing the green line at 5,350 itself excited the flame feebly but definitely (1.4 per cent).

These results with thallium would seem to be related very intimately with those on the excitation of sodium vapor by means of the *D* lines and the 303 line of sodium recently described by Strutt,[1] The effect may thus be designated as resonance radiation, in the broader sense in which that term is frequently used,[2] but not in the restricted sense proposed by Franck. The narrowing of the bands by exposure of the flame to the exciting light is, however, a matter which demands further experimental study.

[1] R. J. Strutt. Proc. Roy. Soc., XCVI, p. 272, 1920-21.
[2] See Foote and Mohler, Origin of Spectra, 1922, p. 90.

CHAPTER X

LUMINESCENCE OF INCANDESCENT SOLIDS

I. THE BLUE GLOW

[Based on experiments by E. L. Nichols and H. L. Howes.]

Certain oxides when heated to incandescence emit light of a distinctly bluish cast at temperatures corresponding to the dull-red heat of non-selective radiators. To this effect, which is particularly well marked when the heating is done with a hydrogen flame sufficiently reinforced with oxygen to secure the desired temperature, we have given the name of *blue glow*. It is a special case of the luminescence of incandescent solids, a topic which, in its broader aspects, will form the subject of this chapter.

In our study of the blue glow it was desired to determine (1) the temperature of the glowing oxide; (2) the brightness of its temperature radiation proper; and (3) the brightness of the *blue glow* itself, which may be regarded as superimposed upon the temperature radiation.

For this purpose we used an optical pyrometer of the type based upon the well-known Morse gage, in which the filament of an incandescent lamp in the eye-piece of the instrument is superimposed upon the image of the glowing surface the temperature of which is to be measured. To mount the oxide for observation an annular groove about 1 cm. in outer diameter, 1 mm. deep, and 2 mm. wide was ground in a bed of alundum. Fragments of thick-walled alundum tubing of large diameter, of which an abundance chanced to be available, answered admirably for this purpose. The annular groove (fig. 125) was pressed full of the black oxide of uranium, a substance which affords an excellent approximation to the ideal black body[2] and which withstands the direct contact of the H-O flame better than any black powder which we have thus far found. The disk of alundum within this ring of uranium oxide was then covered with the oxide to be studied, the two surfaces of powder being carefully pressed down to the same level. Especial care was taken to have a sharp boundary-line between the white oxide within and the ring of black powder surrounding it. Upon the surface thus prepared

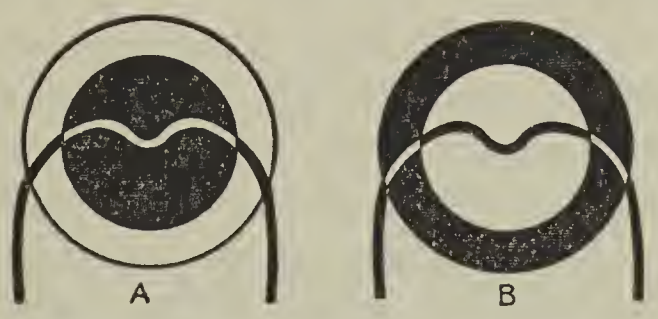


FIG. 125—The pyrometer field

[1] Nichols and Howes. Jour. Opt. Soc. Am., VI, p. 42–53, 1922.

[2] Experiments substantiating this statement will be found in an earlier chapter (see Chapter VIII.)

a flame of hydrogen from a blast-lamp, with just sufficient oxygen to give it direction and stability, played vertically and concentrically from above. It was found that when the two surfaces were at the same level, neither being sensibly elevated or depressed with reference to the other, and when the flame was large enough to cover them fully and was properly centered, they attained the same temperature. Thus the brightness I_0 of the incandescent oxide under observation could be compared with the brightness I_{bb} of a black body at the same temperature. (Both I_0 and I_{bb} were expressed in terms of the brightness of the black body at 1000° C., which was taken as a convenient arbitrary unit. The relative brightness of the luminescent oxide was given by the ratio I_0/I_{bb}.) The most satisfactory arrangement was found to be that indicated in figure 125, *B*, where the black ring represents the surface of uranium oxide and the inner disk a coating of the oxide to be studied. The image of the filament of the pyrometer lamp is seen against this pattern.

At the red heat, say 700° C., since these white oxides are exceedingly poor radiators, temperature radiation alone would give us the condition shown in figure 125, *A*, where the disk of white oxide is dark compared with the surrounding ring of black oxide and where the filament may be brought to a degree of incandescence such as to be dark against the black-body background and bright against the central disk. Luminescence of sufficient intensity will reverse this effect, as in figure 125, *B*.

When, as is frequently the case, the luminescence is confined to one end of the spectrum, both appearances may be observed in the same specimen by shifting the color-screen in the eye-piece from red to blue.

To express these conditions and their changes with rising temperature in quantitative form, the following cycle of readings was made at intervals of 50° or less between 600° C. and 1600° C. or up to the point of fusion of the oxide under observation:

(*a*) A setting on the outer ring through the red screen (equivalent wave-length 0.65μ). This gave the *actual black-body temperature* of the black surface, which was the same as that of the oxide of the central disk.

(*b*) A setting on the central disk through the red screen. This gave the black-body temperature corresponding to the red radiation from the oxide of the central disk.

Since, as has already been mentioned, the oxides in question are exceedingly feeble temperature radiators, and since the blue glow is of too short wave-lengths to pass the red screen, these measurements, for the lower portion of our range of temperature, *i. e.*, below 1000° C., gave black-body temperatures far below the actual temperature of the surface.

(*c*) A setting upon the central disk seen through a solution of ammonio-sulphate of copper which absorbed all red and yellow rays and practically all of the green of the spectrum. The equivalent wave-length for this screen was about 0.45μ. It transmitted the greater part of the radiation constituting the "blue glow," and since, for the lower range, from 800° downward, the temperature radiation of these wave-lengths was almost too small to measure, this setting, with a very close approximation, gave the *blue glow alone.* At higher temperatures, where the ordinary temperature radiation became appreciable, this setting gave the sum of temperature radiation and blue glow.

From these "temperatures" the intensities were computed for the wave-lengths 0.65μ and 0.45μ, which represented approximately the crest of the light selectively transmitted by the color-screens in the eye-piece of the pyrometer.

The results obtained by measurements of the oxides of calcium, magnesium, beryllium, zirconium, silicon, and aluminum are given in tables LVIII, LIX, and LX.

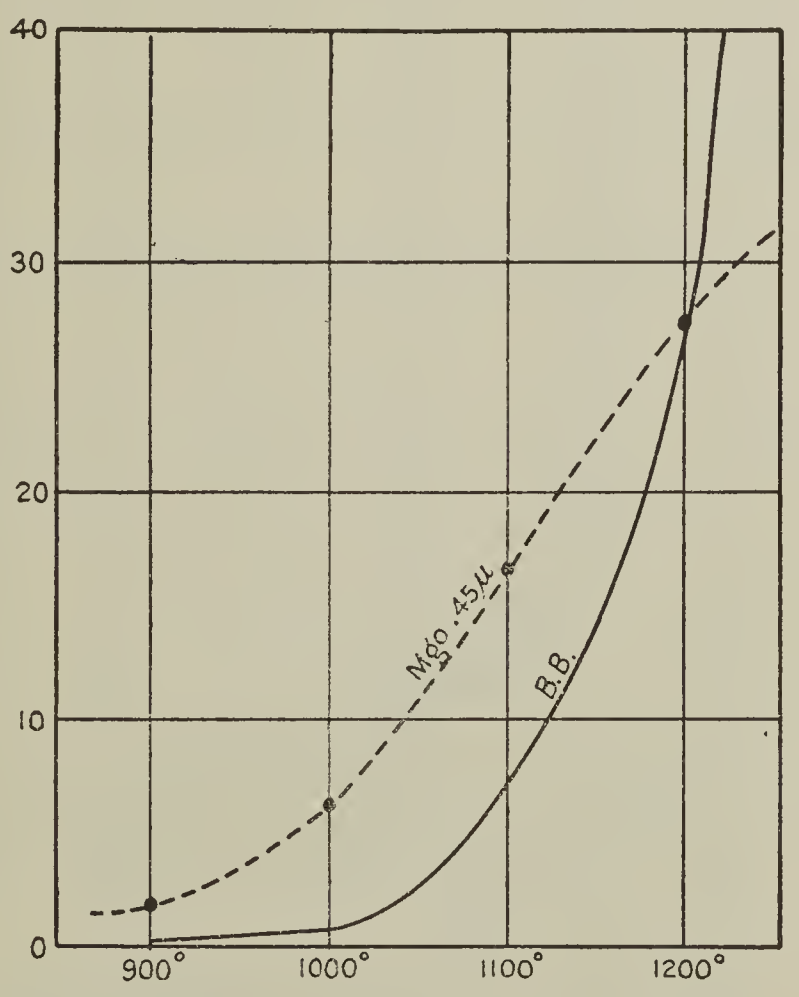


FIG. 126—Blue glow of magnesium oxide, 900° to 1200°

The blue glow is essentially a phenomenon of the lower stages of incandescence. Its upper limit can not be given definitely in degrees, since it depends upon the state of activity of the oxide, but it lies between 1000° and 1200° in the cases thus far studied. If, as in figure 126, we plot the brightness of the blue of the spectrum (0.45μ) of one of these oxides (MgO) between 900° and 1200° and for comparison the brightness curve (black body) for the corresponding region of the spectrum of a black body, we see that the oxide remains *brighter than the black body* until a temperature of about 1200° is reached. It is this excess of radiation above what even a perfect radiator such as the ideal black body is capable of producing by virtue of its temperature alone which constitutes the effect in question.

The lower limit of the blue glow is the temperature threshold of visibility. For the lowest temperature at which we can observe we

get the *maximum value* of the ratio between the brightness of the glow and that of a black body of the same temperature, *i. e.*, I_0/I_{bb}.

In figures 127 and 128 are plotted curves for this ratio for the six oxides in tables LVIII, LIX, and LX. Such a diagram, to this scale, indicates nothing of the phenomenon occurring about 1000°, where the values approach and often fall below unity. Still less can the ratio for the red of the spectrum be thus depicted. The figure shows, however, that:

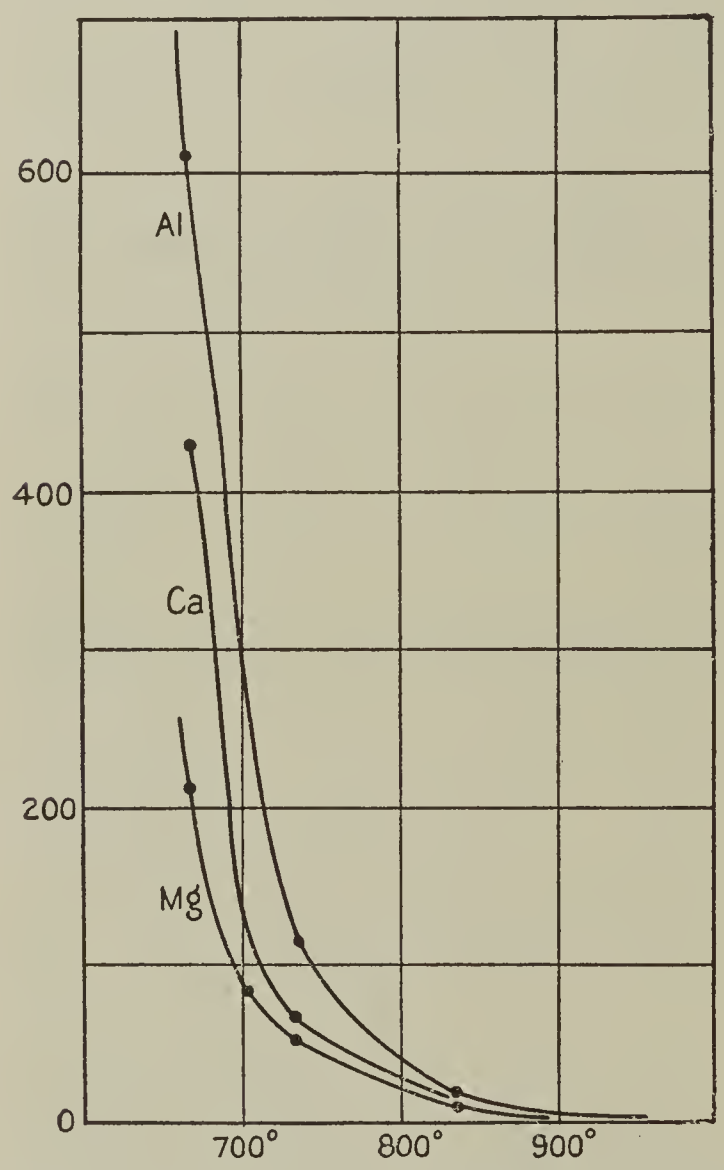


FIG. 127—Three typical curves for the blue glow. Ordinates are ratios of luminescence to black-body radiation for Al_2O_3, CaO, MgO (0.45μ)

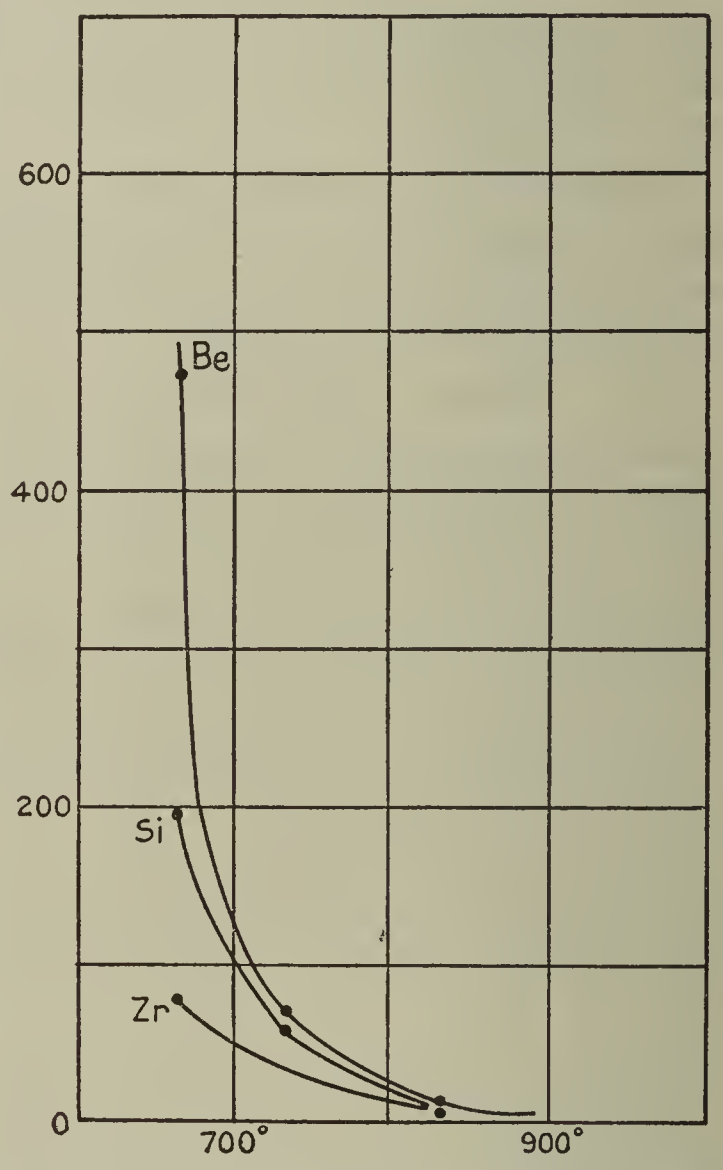


FIG. 128—The blue glow of BeO, SiO_2, ZrO_2. Ordinates are ratios of luminescence to black-body radiation for 0.45μ

(1) The curves for the various oxides are similar as to type.

(2) In no case is there an indication of an approaching maximum in the direction of lower temperatures.

(3) The temperature range within which the brightness of the blue end of the spectrum, to which these curves apply, falls to values of the same order as the corresponding intensity of black-body radiation, is nearly the same for all these oxides.

With logarithms of the intensity ratios as ordinates, we can bring the entire range of temperatures over which measurements were made into one plot and compare the changes occurring in the intensity of the red end of the spectrum with those in the blue.

Figure 129 contains such curves for magnesium oxide, and these are quite typical of all the substances thus far investigated. The characteristics common to all are as follows:

(1) The luminescent outburst, with certain exceptions to be considered later, does not involve the longer wave-lengths.

(2) The radiation in the red, which, at the lower temperatures, is probably all temperature-radiation, rises from very small intensities

FIG. 129—Logarithmic curves for blue glow (0.45μ) and temperature radiation (0.65μ) of MgO. Ordinates are values of $\text{Log}_{10} I_0/I_{bb}$

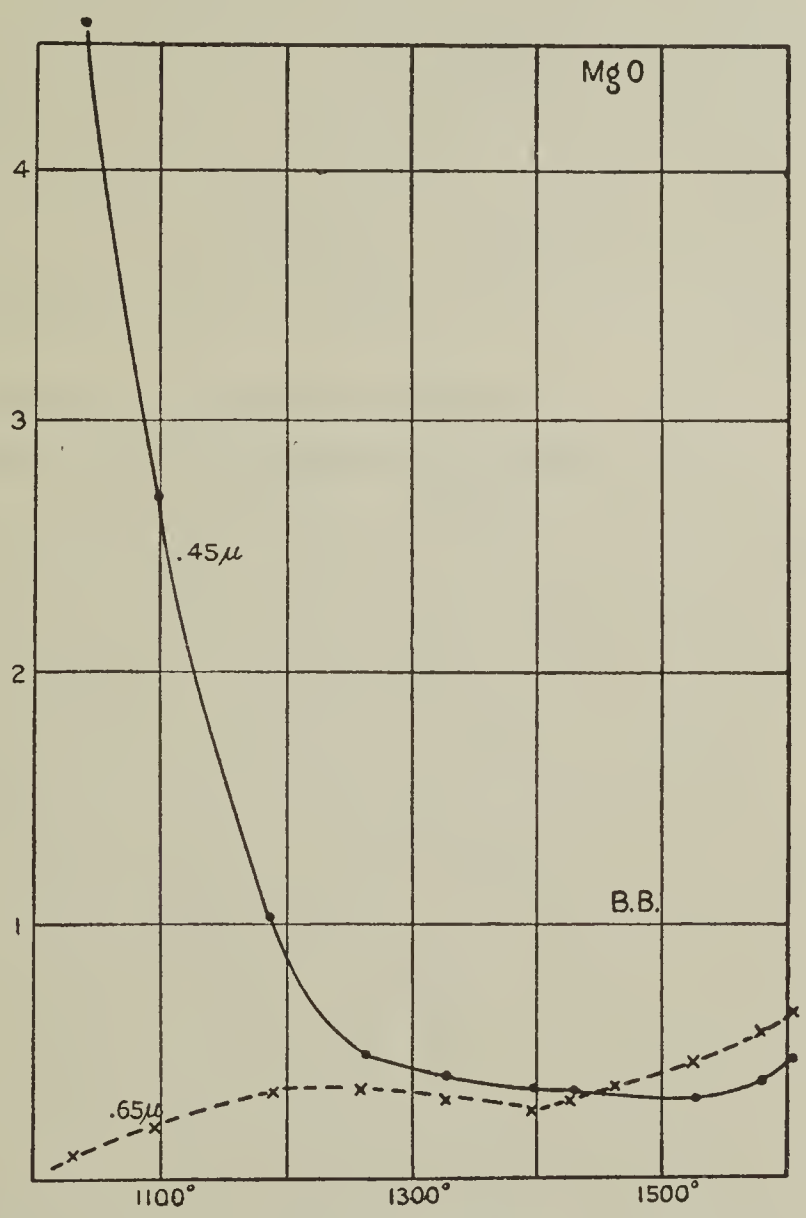


FIG. 130—The radiation of MgO above 1000° C.

and approaches the falling values for the radiation in the blue. Thus the oxide in passing from 600° to 1200° goes over from a body exhibiting blue luminescence and almost no temperature-radiation (for MgO less than a thousandth of that of a black body) to a body radiating almost non-selectively by temperature alone, with a radiating power of the same order as that of the black body.

(3) The logarithmic curve is approximately linear up to the point where temperature-radiation supplants luminescence (1000° to 1200°). The curves for the ratio I_0/I_{bb} in figures 127 and 128 are, then, exponential curves, warped sometimes by changes due to fatigue

during the run and rendered more or less irregular by failures to completely control the conditions.

(4) When temperature radiation has supplanted luminescence (at from 1000° to 1200°) the logarithmic curve tends to become horizontal, indicating that the effect of temperature is now that expressed by the usual equation for black-body radiation.

(5) The knee of the logarithmic curve affords a criterion for the change of temperature radiation and thus serves to locate the upper limit of the blue glow. Comparing figures 126 and 129, we should conclude that luminescence did not altogether cease at the crossing of the curves at 1200°, but continued slightly beyond to a point at which the normal radiating power by temperature had been reached (say at 1260° for MgO in the experiment which these curves illustrate).

II. LUMINESCENCE AT HIGHER TEMPERATURES

In the foregoing paragraphs the blue glow is described as though it were the only form of luminescence occurring above the red heat. More frequently than not there are, however, other manifestations of luminescence within the range covered by our experiments. These either modify or supplant the blue glow at temperatures below 1200° or succeed it when the oxide is still further heated.

Outbursts of luminescence at temperatures between 1000° and 1600° characterize most of the oxides already described, but to depict these graphically it is necessary to use a larger scale. In figures 130 to 136, inclusive, ordinates are increased 200 times as compared with those in figures 127 and 128, while abscissæ remain unchanged. The horizontal line *BB* of ordinate equal to unity, represents the brightness of a black body for the wave-length and temperature in question. This luminescence, expressed in terms of the ratio I_0/I_{bb}, appears quite insignificant when compared with the blue glow, but since the denominator of the ratio increases according to the usual radiation law, the actual intensity of the luminescence is many thousand times greater, as may be seen by reference to the values of I_0 in tables LVIII to LX.

Magnesium oxide—Of the oxides, the blue glow of which has already been considered, the behavior above 1000° of MgO (fig. 130) is the simplest. In this case no further outburst of luminescence appears. Above 1200° both the blue and red regions of the spectrum lie well below the line *BB*, with a relative intensity of the same order for the two ends of the visible spectrum. The upward trend of the two curves (for 0.45μ and 0.65μ) may or may not indicate the approach of a luminescent range above 1600°. Between 1200° and 1600° the oxide changes gradually from a type of radiation in which blue is stronger relatively than red to the opposite. Below 1450°,

where the curves cross, the glowing oxide appears paler than a non-selective radiator of the same temperature; above that temperature it appears more ruddy. It will be seen from figures 131, 132, 133, 134, and 136 that this is characteristic of all of this group of oxides excepting SiO_2.

Berylium oxide—The characteristic feature in the diagram (fig. 131) for this substance is the very sudden tenfold accession of brightness at 1200° and the return to what is probably temperature radiation at about 1400°. The change from blueness at 1100° to ruddiness above 1300° is also striking.

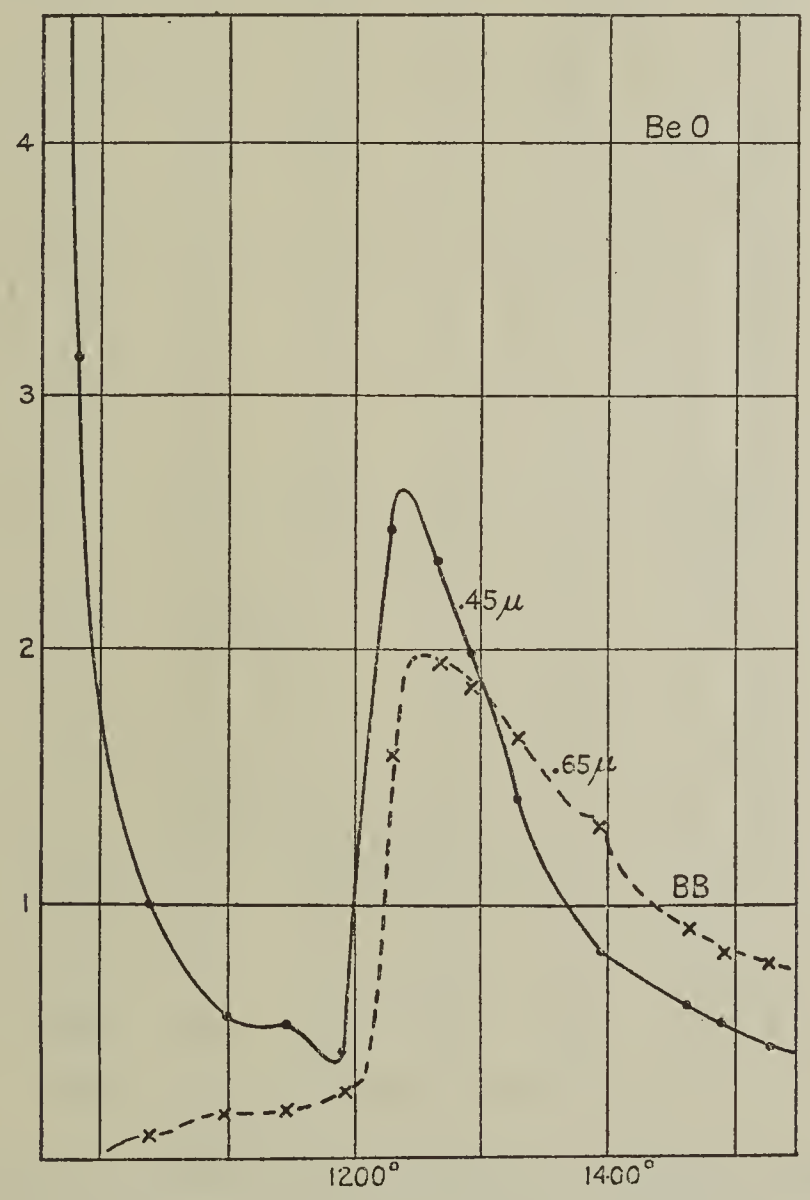


FIG. 131—The outburst of luminescence in BeO at 1200° C.

Calcium oxide—The two crests upon the descending curve for 0.45μ are, as will be seen later, characteristic of this oxide. The red of the spectrum nowhere rises above the *BB* line, but above 1375° we have the transition from the blue to the ruddy type of incandescence. These curves for I_0/I_{bb} do not indicate explicitly whether at any point there is an actual falling off in I_0 or whether, as in the case of MgO (fig. 130), the rise in intensity after passing the crest of the outburst of luminescence is merely retarded. In the radiation from CaO we have both effects, as may be seen in figure 132, which gives the changes of I_0 with temperature. The crest just below 1300°

here appears as a slight upward deviation of the radiation curve, whereas at 1400° the curve trends sharply downward, so that *the brightness of the oxide at 1425°, taking the sum of temperature radiation and luminescence, is scarcely more than half* (190 : 350) *of the brightness at 1325°*. This is an impressive demonstration of the substantial character of the superimposed luminescence.

Zirconium oxide is of the same type as to its luminescence as CaO, but with the two crests of the curve for 0.45μ shifted 150° toward

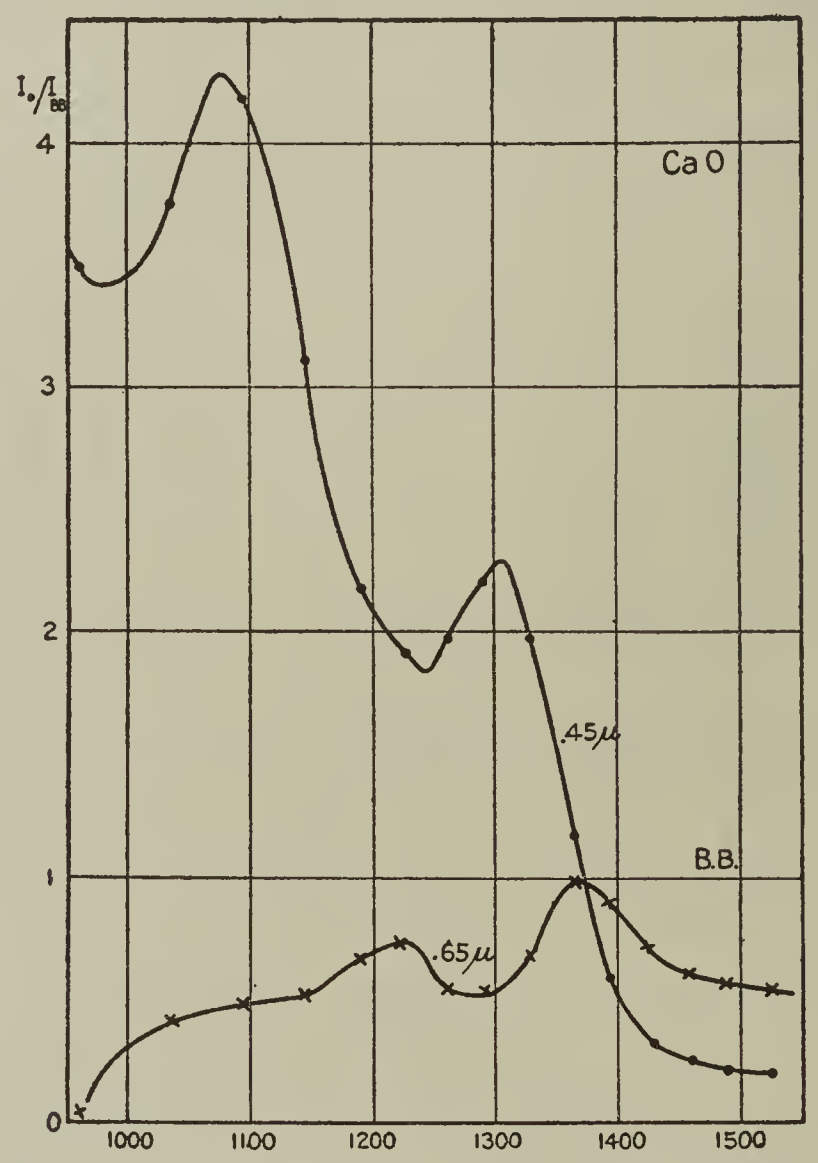


FIG. 132—Radiation from CaO above 1000°

high temperatures (1075° to 1225° and 1300° to 1450° respectively). In the case of the crest at 1450°, moreover, the red end of the spectrum is more in evidence than the blue.

Silicon oxide and aluminum oxide—These two oxides are of particular interest in that their diagrams afford the first definite clue to a relation between the outbursts of luminescence and transformation points in the glowing substance. The temperature of the chief crest in the curve for 0.45μ in figure 135 (SiO_2) lies just above 1400° and the outburst is almost entirely comprised between the limits of 1300° to 1500°. It seems natural to associate it with the well-established transformation point of quartz. In the case of alumina also (fig. 136) we have two crests, a minor one at 1160° to 1175° and the notable maxi-

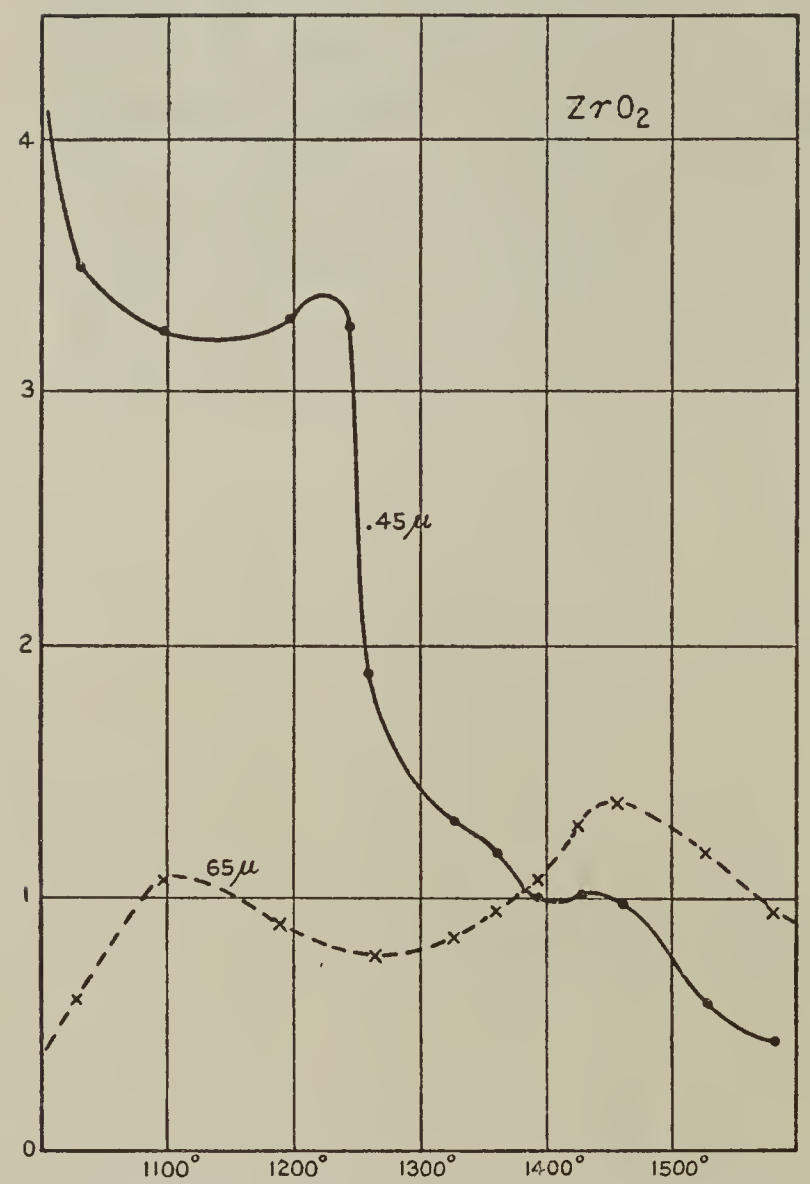
mum at 1410° involving chiefly the longer wave-lengths, *i. e.*, the radiation capable of passing the red screen in the eye-piece of the pyrometer. Both of these are associated with transformation points. The lower crest occurs where the resistivity curves of Northrup for alundum *show an inflection.* Northrup,[1] in his paper, declared his inability to explain this inflection, but wisely refused to ignore it. The chief maximum corresponds similarly to irregularities in the relation between temperature and resistivity, published by Hering[2] from Northrup's data. Figure 137 gives this curve plotted to two scales, which show the breaks occurring at about the same interval below the crest.

FIG. 133—Radiation from CaO compared with that of a black body

We have stated in Chapter VIII that zinc oxide when excited by the hydrogen flame begins to show a red band at 568°, which at 700° is displaced by a yellow-green band, which, in turn, disappears at 940°. Measurements of the brightness with an optical pyrometer show that the luminescence of the zinc oxide reached a maximum of brightness somewhat above 800° when it was about 11.4 times as bright as copper oxide (taken as a black body) at the same tempera-

[1] E. F. Northrup. Metallurgical and Chemical Engineering, XII, p. 125, 1914.
[2] Carl Hering. Metallurgical and Chemical Engineering, XIII, p. 25, 1915.

ture, and 115 times as bright as zinc oxide at the same temperature when not excited to luminescence by the flame.



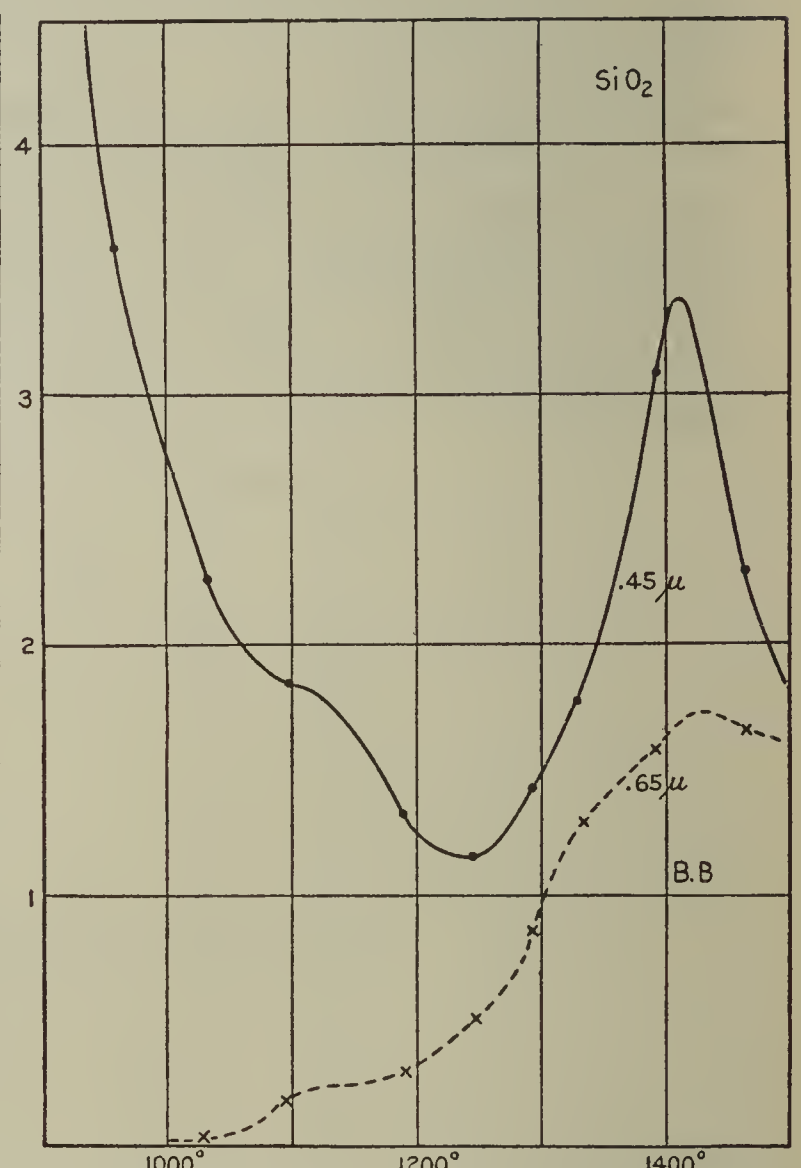


FIG. 134—Radiation from ZrO_2 above 1000° FIG. 135—The luminescent outburst from SiO_2 at 1400°

In the accompanying diagram (fig. 138) curve *L* shows the brightness of zinc oxide under flame excitation compared with its brightness when unexcited. Curve *E* is the relative emissivity, and *F* is a function of the resistance, which is linear up to the break shown. It is to be noted that the relative emissivity of zinc oxide to that of copper oxide as a convenient standard falls to a minimum at the temperature of greatest luminescence and rises rapidly as the luminescence disappears with increasing temperature. Also, the electrical resistivity of zinc oxide, as shown by certain unpublished data obtained by Professor C. C. Bidwell and to which he permits us to refer in this connection, undergoes a sudden change within this temperature range of luminescence, indicative of some molecular transformation.

Germanium oxide,[1] of which very rare substance the writers had a pure sample through the kindness of Professor L. M. Dennis, of the Cornell Department of Chemistry, does not exceed the brightness of

[1] E. L. Nichols. Proc. Nat. Acad. Sci. IX, 248, 1923.

the black body at any incandescent temperature up to its melting-point. Its departures from black-body radiation are, however, very striking.

At the lowest stage of incandescence the red end of the spectrum is of scarcely appreciable brightness (at 800° C. less than four-hundredths of the brightness of the corresponding region in the spectrum of a black body of like temperature), whereas the blue is comparable with the black body (brightness about 100 per cent of that of the same part of the spectrum of the black body). The color of the germanium oxide at the red heat is therefore bluish rather than ruddy.

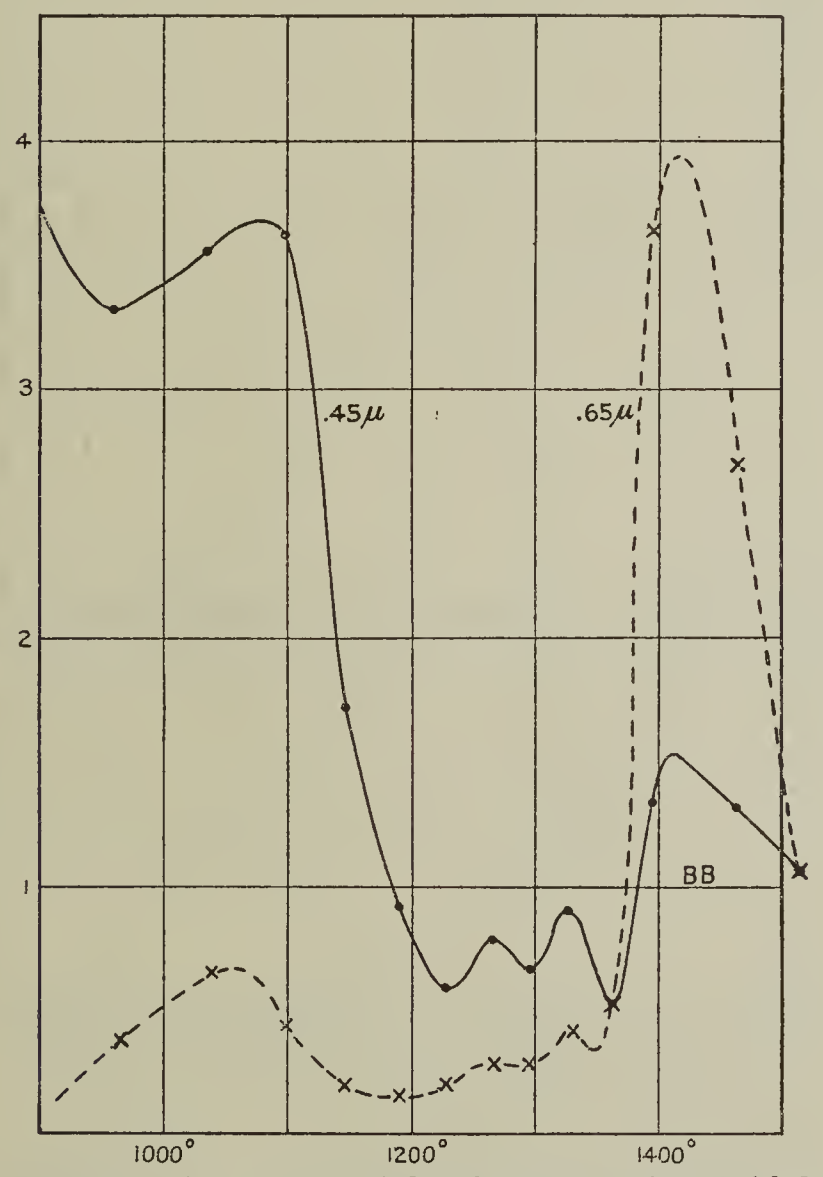


FIG. 136—Outbursts of luminescence from Al_2O_3

With rising temperature the longer wave-lengths increase much more rapidly than the blue and violet, and just above 1200° the distribution of brightness in the spectrum is approximately that of a black body and the tint is neutral. The brightness of the germanium oxide is, however, then less than one-tenth of that of a black body at the same temperature.

At still higher temperatures the red becomes increasingly dominant, and before fusion the red end of the spectrum approaches that of a black body in brightness, while the blue remains relatively weak

(10 per cent of that of the corresponding region in spectrum of a black body). The color of incandescence is then *ruddy* as compared with that of a black body at the same temperature.

These remarkable changes find more definite expression in figure 139 in which abscissæ are temperatures in degrees centigrade, and ordinates are ratios (I_0/I_{bb}) of the brightness of the germanium oxide to that of the corresponding region in the spectrum of the

FIG. 137—Conductivity of aluminum oxide

uranium oxide at the same temperature. Since the radiation of the latter is very nearly equal to the black-body radiation, the above ratio may, for present purposes, be considered as the relative brightness of the germanium oxide in terms of the corresponding brightness for similar wave-length and temperature of the black body taken as unity.

As in all the incandescent oxides thus far studied, the visible radiation of germanium oxide depends not only upon the temperature, but also to a considerable extent upon the mode of heating, particularly as to the abundance or paucity of free oxygen in the flame and upon the previous heat treatment, etc. The values given in table

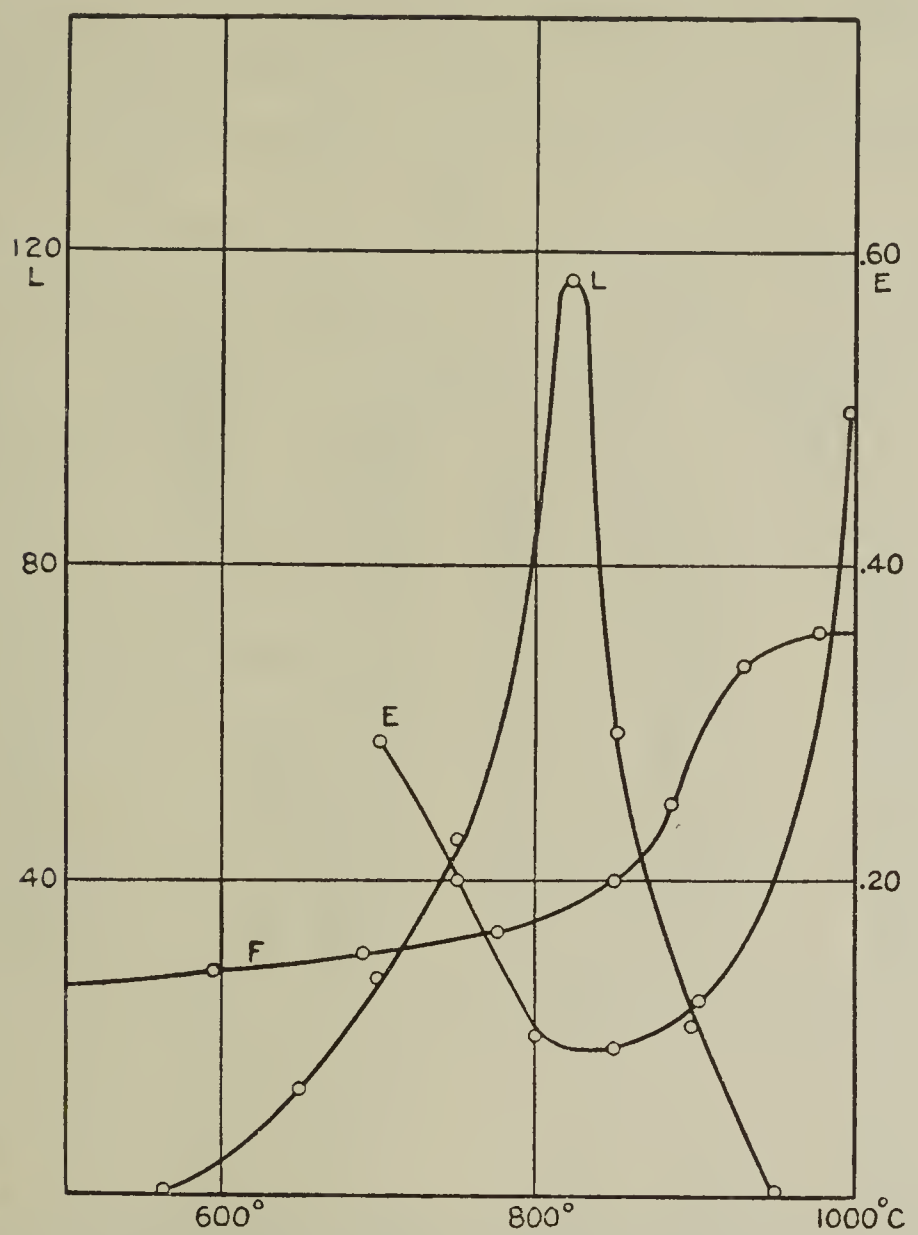


FIG. 138—Brightness and emissivity of zinc oxide

TABLE LVIII—*The incandescence of magnesium and beryllium oxides*

Temp., C.	I_{bb}	MgO				BeO			
		I_0		I_0/I_{bb}		I_0		I_0/I_{bb}	
		0.65μ	0.45μ	0.65μ	0.45μ	0.65μ	0.45μ	0.65μ	0.45μ
665	0.00013	0.00000018	0.0202	0.00140	156.7	0.000000025	0.0563	0.000195	437.0
735	.00123	.0000026	.0320	.00214	45.0	.0000016	.0795	.000867	65.8
837	.0246	.00033	.423	.0135	17.2	.00067	.295	.0271	12.0
960	.419	.0202	3.63	.0482	8.77	.038	1.44	.0382	3.14
1,037	1.95	.165	8.91	.0847	4.57	.213	1.95	.109	1.00
1,097	5.93	1.077	16.1	.182	2.72	1.00	3.31	.169	.561
1,145	13.2	.....	.....	.....	.....	2.46	6.37	.186	.511
1,190	26.6	9.77	26.4	.367	1.04	6.75	13.0	.252	.423
1,228	45.7	.....	.....	.....	.....	72.5	110.2	1.58	2.44
1,263	76.7	26.6	36.7	.347	.479	146	179.9	1.91	2.35
1,294	156	.....	.....	.....	.....	229	230	1.98	1.99
1,328	178	55.6	72.0	.312	.404	295	254	1.66	1.43
1,394	389	62.0	139	.357	.356	513	316	1.32	.813
1,429	582	182	194	.313	.333	.....	.....	.....	.....
1,462	828	285	277	.344	.334	767	513	.927	.621
1,488	1,097	.....	.....	.....	.....	910	600	.830	.535
1,527	1,602	745	525	.460	.324	1,181	773	.728	.477
1,580	2,690	1,614	1,012	.600	.375	1,641	1,052	.610	.391
1,606	3,420	2,309	1,387	.675	.406	1,928	1,282	.564	.375

TABLE LIX—*The incandescence of calcium and zirconium oxides*

Temp., C.	I_{bb}	CaO				ZrO_2			
		I_0		I_0/I_{bb}		I_0		I_0/I_{bb}	
		0.65μ	0.45μ	0.65μ	0.45μ	0.65μ	0.45μ	0.65μ	0.45μ
665	0.00013	0.00000055	0.0276	0.00432	216	0.0000026	0.0068	0.0204	53.1
735	.00123	.0000159	.0632	.0128	52.2	.000077	.0382	.0621	30.9
837	.0246	.00292	.336	.114	13.7	.0039	.403	1.61	16.4
960	.419	.100	1.46	.240	3.49	.121	3.41	.288	8.15
1,037	1.95	.802	7.31	.411	3.75	1.20	69.1	.617	3.50
1,097	5.93	2.62	25.0	.453	4.19	6.34	19.2	1.07	3.25
1,145	13.2	6.92	41.7	.522	3.11	.....	.....	.....	.....
1,190	26.6	17.5	58.2	.656	2.18	24.5	87.5	.923	3.29
1,228	45.7	33.1	87.5	.725	1.91	.....	.....	.....	.....
1,263	76.7	40.7	151	.531	1.97	59.0	146	.770	1.91
1,294	156	61.7	254	.535	2.20	.....	.....	.....	.....
1,328	178	120	351	.671	1.97	155	233	.870	1.31
1,362	266	264	310	.994	1.17	254	317	.979	1.19
1,394	389	345	226	.887	.582	419	397	1.07	1.00
1,429	528	422	190	.725	.326	769	610	1.32	1.04
1,462	828	507	226	.613	.274	1,150	798	1.38	.990
1,488	1,097	624	126	.570	.115	.....	.....	.....	.....
1,527	1,602	871	327	.536	.202	1,950	1,102	1.20	.679
1,580	2,690	1,225	578	.455	.215	2,620	1,500	.973	.427
1,606	3,420	1,429	794	.381	.232	.....	.....	.....	.....

TABLE LX—*The incandescence of silicon and aluminum oxides*

Temp., C.	I_{bb}	SiO_2				Al_2O_3			
		I_0		I_0/I_{bb}		I_0		I_0/I_{bb}	
		0.65μ	0.45μ	0.65μ	0.45μ	0.65μ	0.45μ	0.65μ	0.45μ
665	0.00013	0.000000076	0.0382	0.00059	195	0.000000051	0.0794	0.00039	617
735	.00123	.0000026	.0708	.00210	57.3	.0000036	.144	.00287	117
837	.0246	.00059	.341	.0239	13.9	.000209	.422	.00851	17.2
960	.419	.0275	1.65	.0600	3.59	.0121	.733	.0287	1.74
1,037	1.95	.191	4.42	.0977	2.26	.159	1.66	.0813	.852
1,097	5.93	1.10	11.0	.186	1.86	.912	3.76	.154	.634
1,145	13.2	.....	.....	.....	.....	2.72	7.41	.206	.573
1,190	26.6	8.51	35.3	.316	1.33	7.76	24.5	.292	.923
1,263	76.7	41.2	89.1	.537	1.16	32.2	103.5	.420	1.35
1,294	156	100.0	167	.865	1.44	64.6	155	.595	1.34
1,328	178	233	316	1.31	1.77	133.4	195	.748	1.09
1,362	266	.....	.....	.....	.....	251.0	298	.944	1.12
1,394	389	614	631	1.58	3.09	408	582	1.048	1.49
1,462	828	1,390	1,902	1.68	2.30	1,000	1,084	1.21	1.31
1,527	1,602	2,500	2,566	1.54	1.55	2,370	1,863	1.46	1.15

LXI and shown graphically in figure 139 are for a sample previously heated to incipient fusion. Successive runs repeat themselves in kind, but not in every detail; the curves in figure 139 are, however, typical.

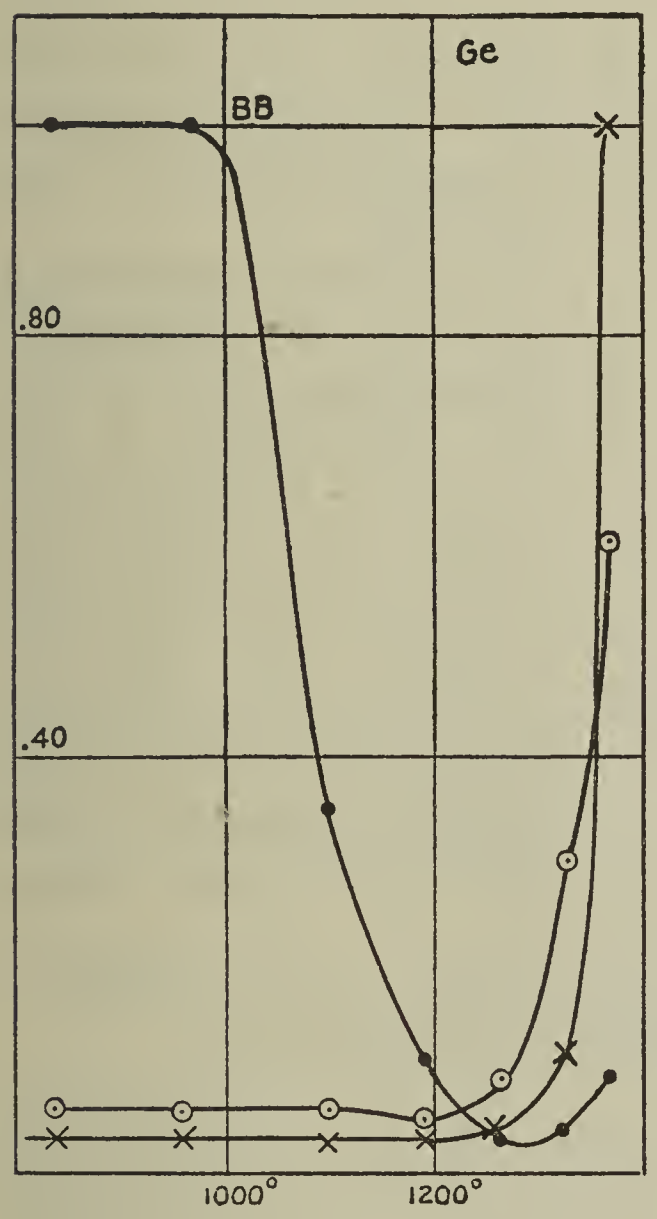


FIG. 139—Visible radiation from germanium oxide (reversal of color)

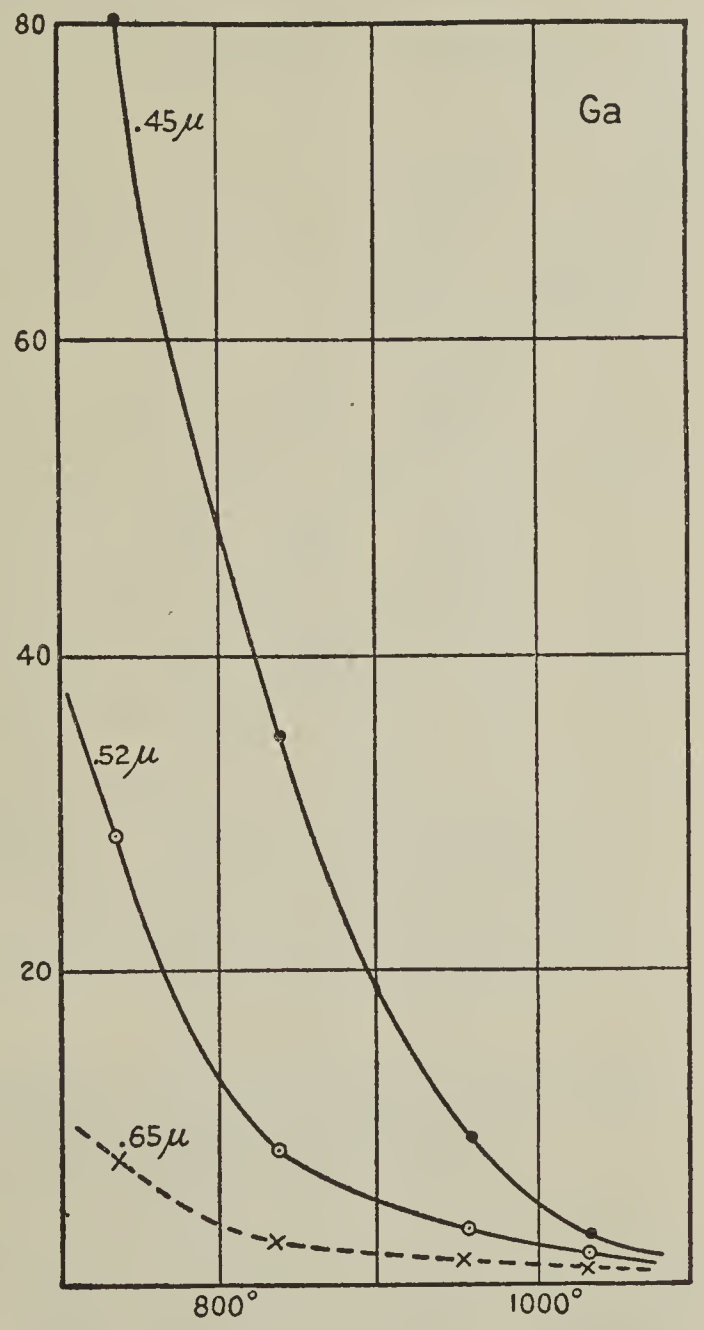


FIG. 140—The modified blue glow of gallium oxide

TABLE LXI—*Visible radiation from germanium oxide*

Temp. °C	I_{bb}	I_0			I_0/I_{bb}		
		.65μ	.52μ	.45μ	.65μ	.52μ	.45μ
837	0.0246	0.000937	0.0274	0.0306	0.036	0.112	1.000
960	.419	.0161	.0279	.4172	.038	.067	1.000
1,097	1.950	.232	.4170	2.230	.039	.076	.354
1,190	26.60	1.120	1.720	2.742	.042	.065	.112
1,263	76.70	2.780	7.642	2.759	.036	.100	.036
1,328	178.0	19.10	43.70	7.386	.118	.251	.042
1,370	268.0	296.0	175.0	28.23	1.000	.608	.095

Preponderance of blue at the lower temperatures and of red as fusion is approached are constant features and the temperature at which the intensity curves for these regions cross each other appears to be always the same. What changes of physical condition accompany this reversal we do not know, as no studies of the electrical and other properties of germanium oxide through this range of temperatures have as yet been made.

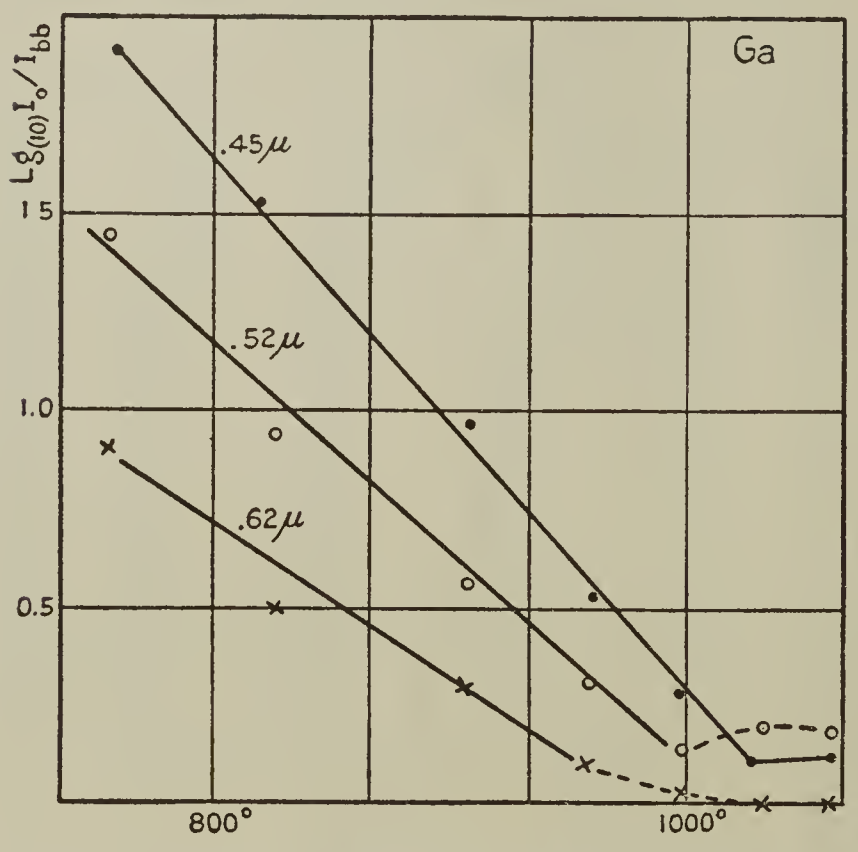


FIG. 141—$Log_{10}I_o/I_{bb}$ and temperature for gallium oxide (cf. with fig. 129)

The sudden accession of brightness at temperatures approaching the melting-point is certainly of the nature of a transformation outburst, the transformation here being from solid to molten form. Probably under proper conditions the intensities, as in the oxides previously studied, would rise to much higher values.

III. LUMINESCENCE OF CERTAIN INCANDESCENT RARE EARTHS, AND OF THE OXIDES OF CERIUM AND PRÆSODYMIUM

Following the study of the six oxides just described, measurements were made upon certain rare earths of which sufficient quantities were available to admit of the application of our method. To gain a somewhat more adequate information of the intensity of radiation from different parts of the visible spectrum, observations were made through a screen transmitting the green (equivalent wave-length 0.52μ) in addition to those for the red and blue previously employed. The results are given in tables LXII to LXIV.

Of these rare earths, *gallium oxide* presents the spectacle (fig. 140) of a modified glow in which the entire spectrum takes part, the regions seen through the red and green screens, as well as the blue, being above the black body in intensity to 1100°. The curves for 0.45μ, 0.52μ, and 0.65μ are all approximately logarithmic until 1000° is past, as appears in figure 141. Above that temperature are two crests in which the green is dominant. (See fig. 142, where ordinates, as in similar previous cases, are magnified 200 times.)

In the case of *samarium oxide,* the blue glow is also somewhat

modified. (fig. 143.) The ratio I_0/I_{bb} is of the same order for blue and for green between 900° and 1200°. The red component is subordinate throughout the range of the diagram. There is a distinct maximum of blue and green just above 900°.

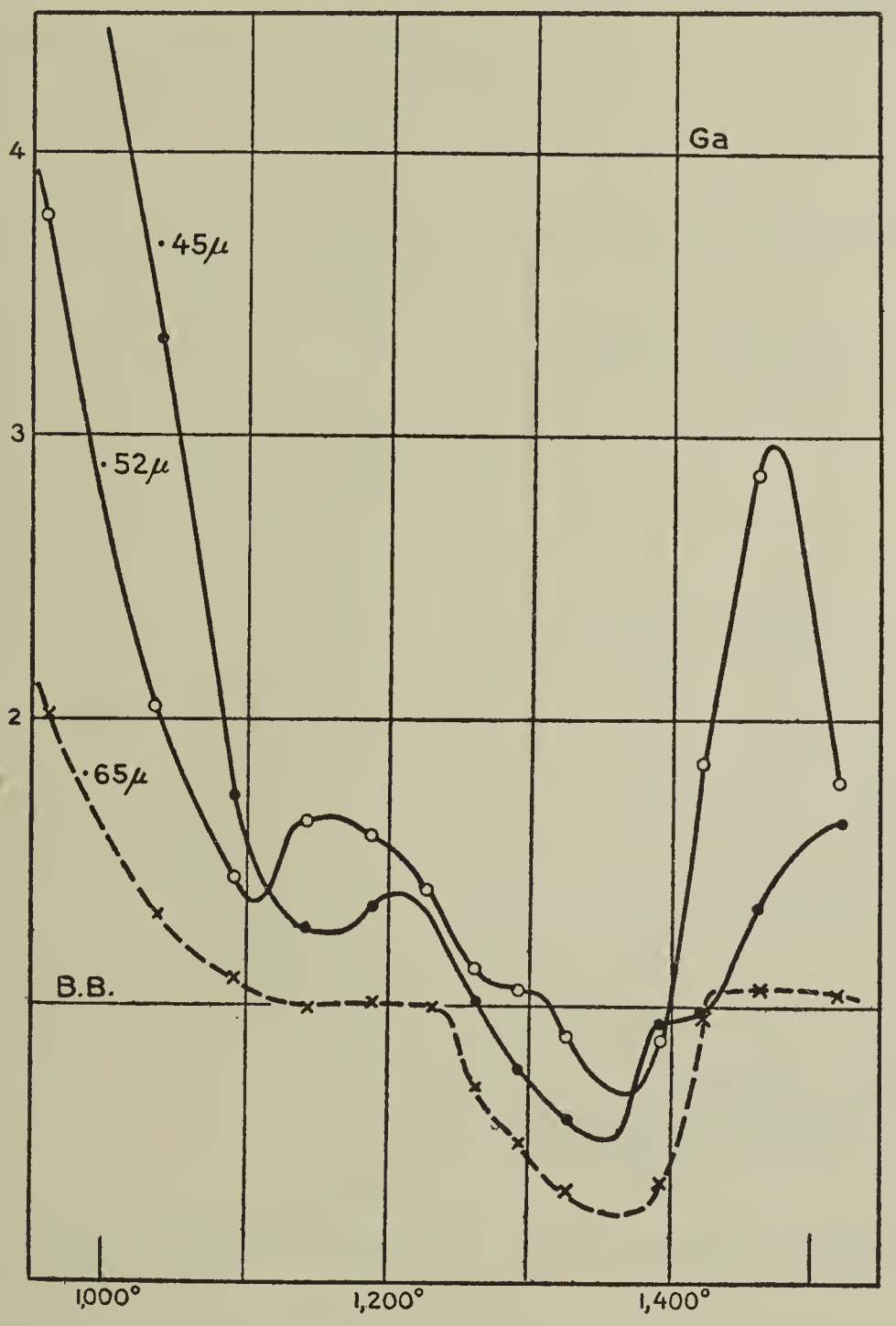


FIG. 142—Radiation from gallium oxide

The curves for this oxide above 1000° (fig. 144) are of unusual complexity. There is evidence of two distinct bands in the spectrum. One, in the blue, as seen through the screen 0.45μ, has a maximum at about 1160°. The other, portions of which are visible through both red and green screens, has a maximum just above 1200°. Evidently the edge of the blue band extends far enough toward the longer wavelengths to be visible to some extent through the other two screens, which accounts for the shoulders on the curves for 0.52μ and 0.65μ.

The same argument leads to the conclusion that the red-green band does not encroach greatly upon the region viewed through screen

0.45μ, since the curve for that wave-length does not show the influence of the crest at 1225°.

An important bearing of these curves for samarium upon the nature of the phenomenon of high-temperature luminescence is discussed in a later paragraph.

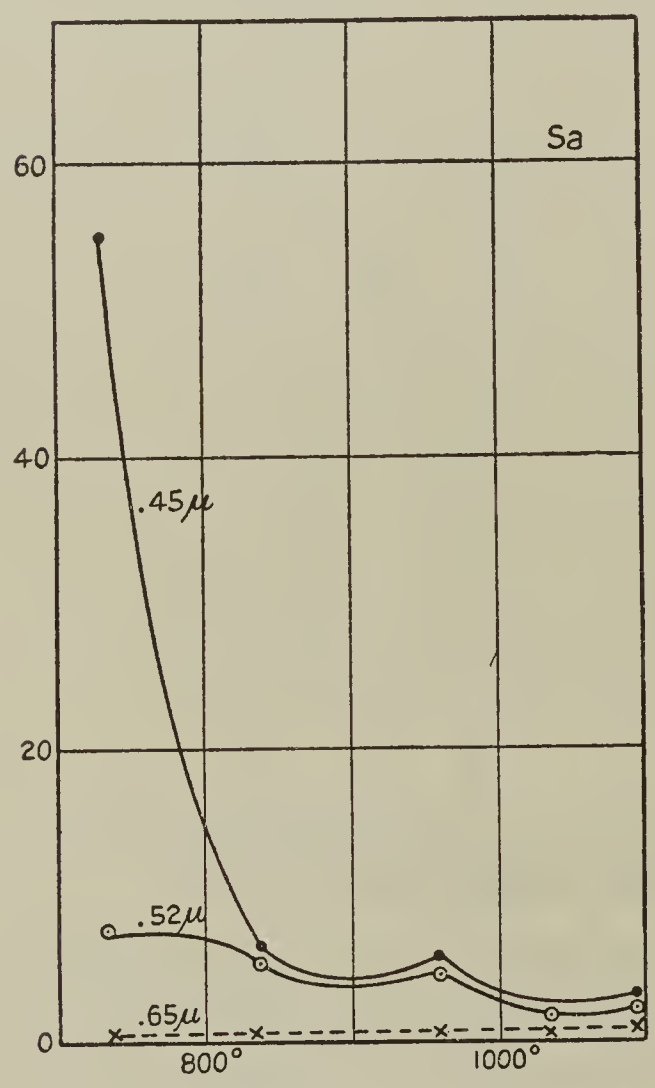


Fig. 143—Radiation from samarium oxide below 1000°

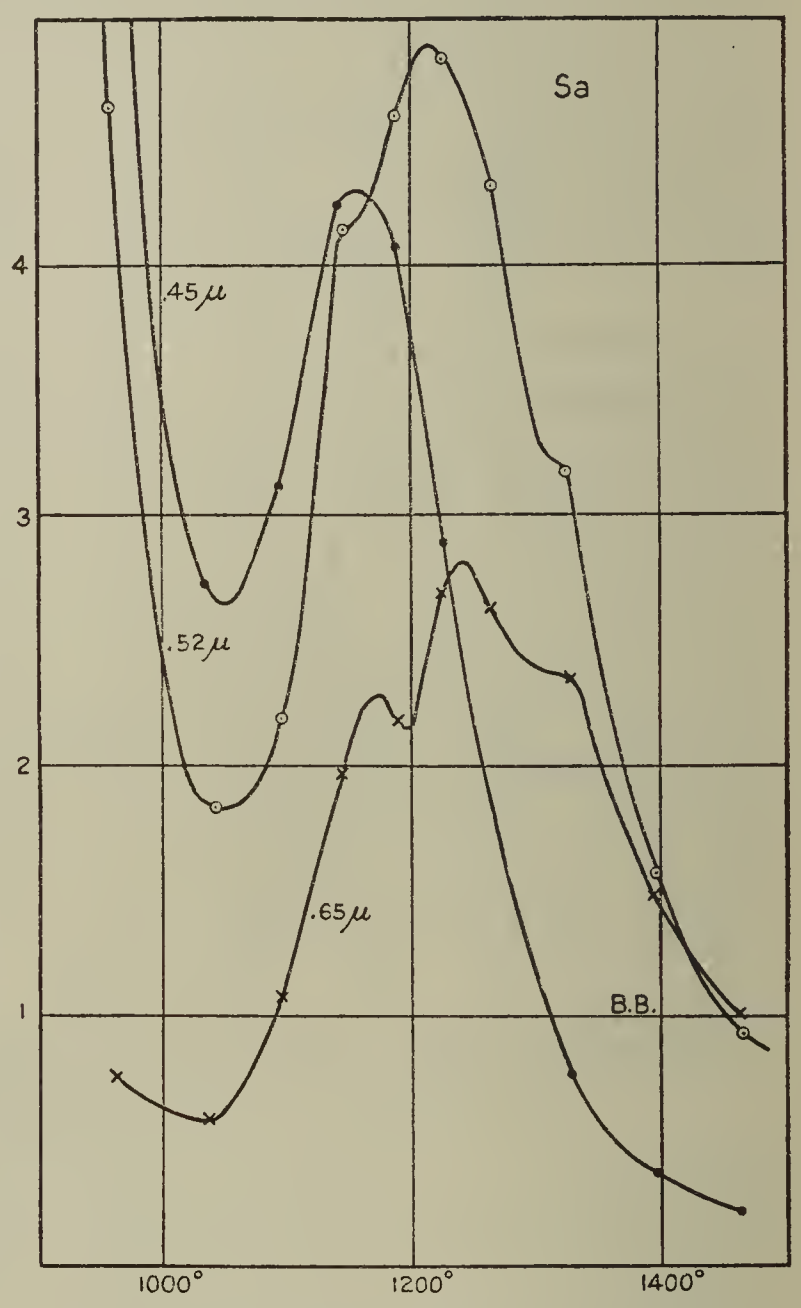


Fig. 144—Radiation from samarium oxide above 1000°

The curves for *gadolinium oxide* (fig. 145) show a blue glow of small intensity, well-defined outbursts involving the entire spectrum at 1000° and 1325°.

In the case of *præsodymium oxide* (fig. 146), which for convenience we may class among the rare earths, there is merely a suggestion, in the upward trend at 735° of the curves for 0.45μ and 0.52μ, of the possible existence of a feeble glow at temperatures too low to admit of measurements. A well-marked crest involving the blue and violet occurs at 960° and a less prominent one in which the green and red are dominant at 1200°. We shall have occasion to refer to the former outburst later on.

The oxide of the companion element *neodymium,* which, because

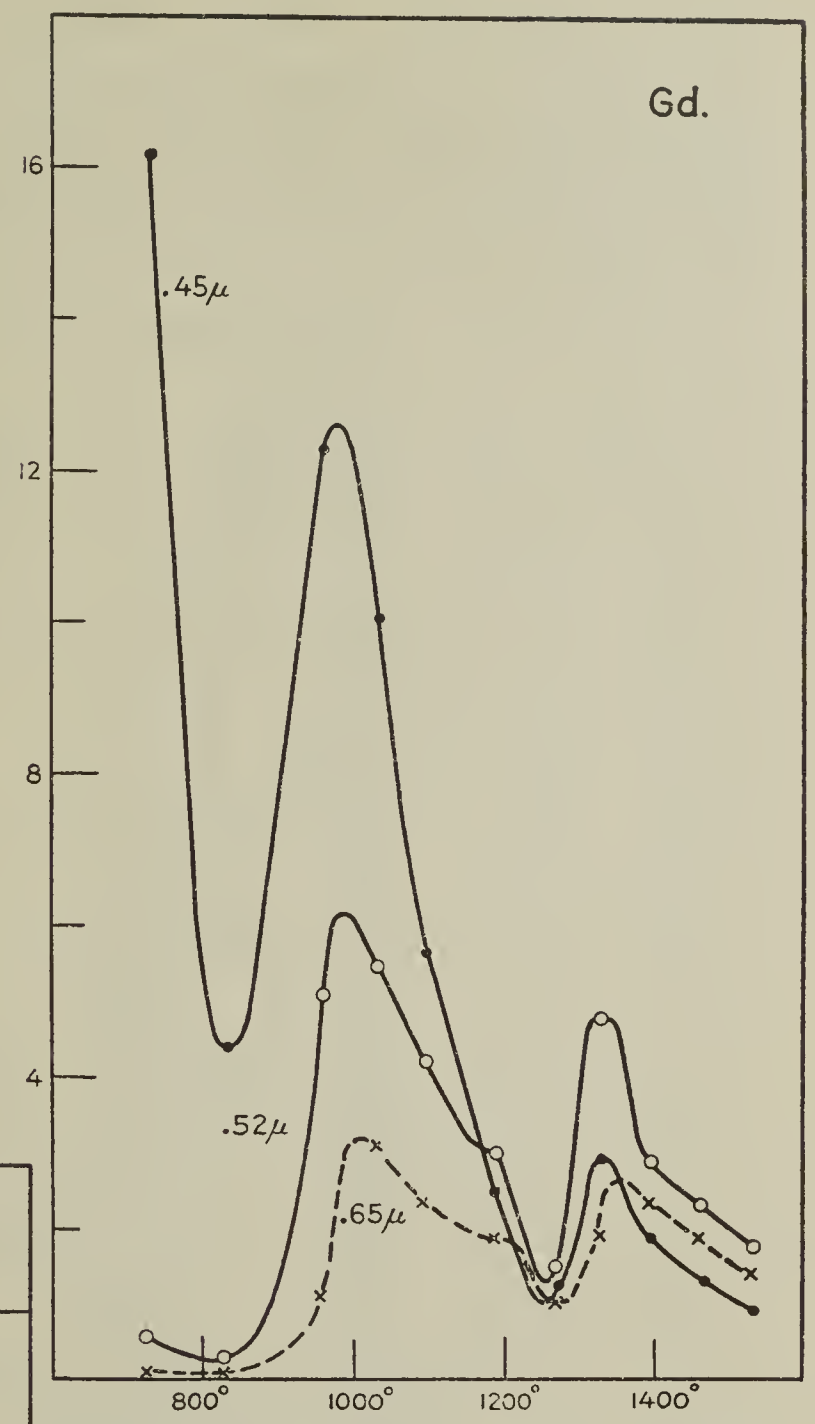


FIG. 145—Outbursts of luminescence from gadolinium oxide

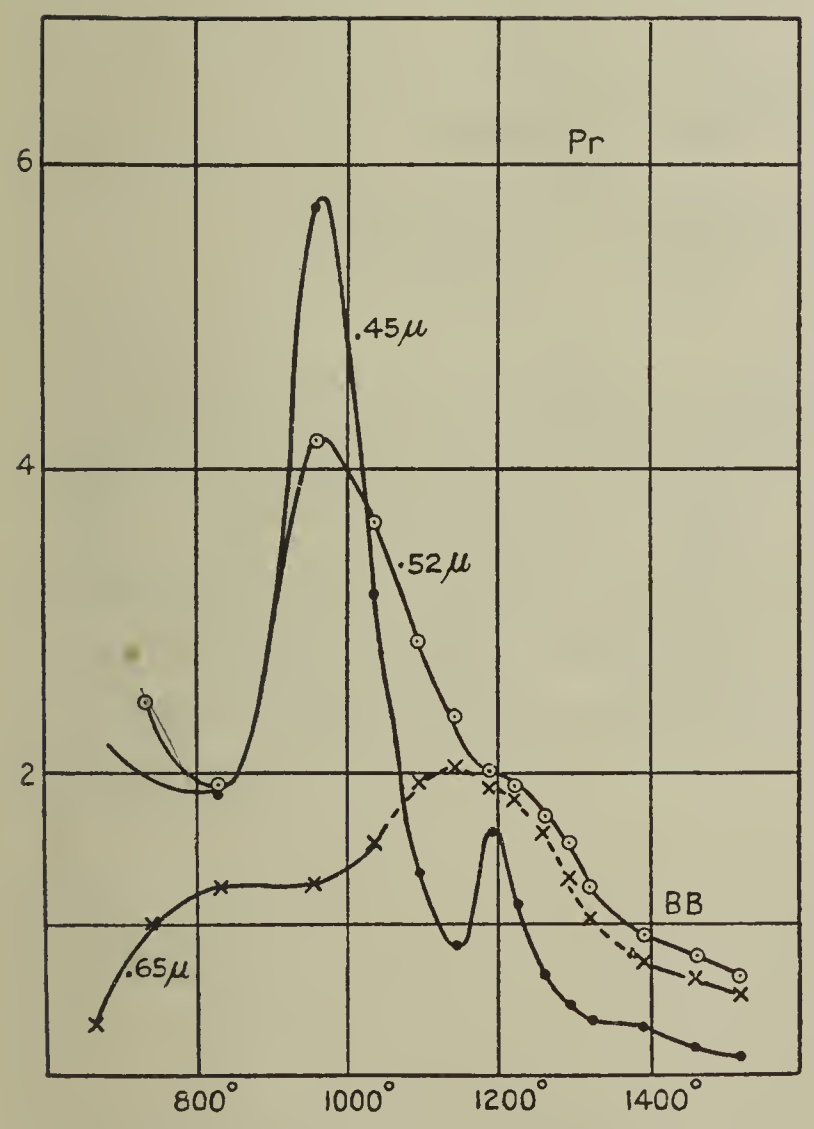


FIG. 146—Outbursts of luminescence from præsodymium oxide

of its well-known emission bands would seem to be better adapted to study by a spectrophotometer than by the use of screens, was reserved for such treatment after a cursory examination with the pyrometer. An account of the somewhat detailed investigation will be found in section VII of this chapter.

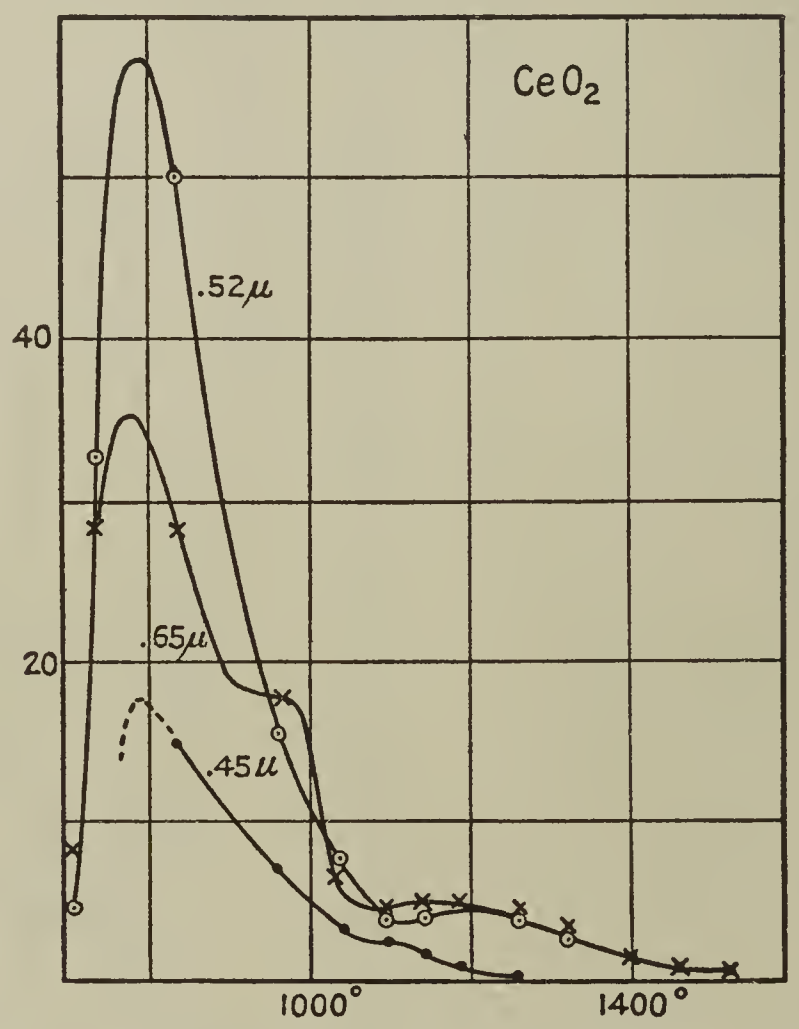


Fig. 147—An outburst of luminescence from cerium oxide at 800° affecting chiefly the longer wavelengths of the spectrum

Cerium oxide is the only substance included in the present investigation which, when heated in the hydrogen flame, gave no indication even of a modified blue glow. In the very marked outburst at 800° green and red are dominant, the blue comparatively feeble, and although measurements were carried down to 702°, at which temperature the field viewed through the 0.45μ screen was too weak to permit of settings, there was no indication of an upward trend of any of the curves. (See fig. 147.)

TABLE LXII—*Incandescence of gallium oxide, samarium oxide, and gadolinium oxide*

Substance	Temp. °C.	I_0			I_0/I_{bb}		
		Red	Green	Blue	Red	Green	Blue
GaO.....	735	0.0100	0.0347	0.100	8.08	28.1	80.2
	837	.0733	.209	.851	2.99	8.51	34.7
	960	.841	1.59	3.94	2.01	3.79	9.40
	1,037	2.60	4.07	6.53	1.32	2.05	3.31
	1,097	6.53	8.51	10.2	1.10	1.43	1.73
	1,145	13.2	22.0	16.8	.995	1.67	1.27
	1,190	26.6	41.7	36.3	1.00	1.57	1.36
	1,228	44.7	63.4	62.4	.978	1.38	1.36
	1,263	53.7	86.1	77.6	.700	1.12	1.01
	1,294	59.6	189	89.1	.515	1.03	.771
	1,328	69.2	155	105	.388	.870	.594
	1,394	143	339	359	.367	.871	.923
	1,429	569	1,097	575	.978	1.87	.988
	1,462	871	2,370	1,097	1.05	2.86	1.325
	1,527	1,679	2,849	2,600	1.03	1.76	1.63
	1,555	2,068	3,350	3,429	.980	1.59	1.62
	1,580	2,341	3,590	4,030	.870	1.33	1.50
SmO.....	735	.00049	.0094	.680	.396	7.64	55.1
	837	.0102	.107	1.55	.425	5.47	6.40
	960	.314	1.94	2.40	.750	4.64	5.73
	1,037	1.10	3.56	5.31	.563	1.83	2.72
	1,097	6.31	12.9	18.5	1.06	2.18	3.13
	1,145	25.9	55.0	56.0	1.96	4.15	4.23
	1,190	58.9	122	138	2.21	4.60	4.07
	1,228	123	221	132	2.69	4.83	2.88
	1,263	202	331	135	2.63	4.31	1.76
	1,328	417	502	135	2.34	3.16	.750
	1,394	576	611	145	1.48	1.57	.371
	1,462	828	716	271	1.00	.927	.206
GdO.....	735	.000051	.000708	.0200	.0417	.573	16.2
	837	.000851	.00596	.108	.0347	.243	4.39
	960	.447	2.30	5.14	1.067	5.16	12.3
	1,037	5.27	10.6	17.6	3.16	5.43	9.02
	1,097	13.9	25.0	33.4	2.35	4.21	5.64
	1,190	51.2	80.2	66.1	1.93	3.02	2.48
	1,263	78.5	112	97.7	1.02	1.45	1.27
	1,328	230	552	340	1.99	4.79	2.94
	1,394	902	1,130	726	2.32	2.91	1.86
	1,462	1,556	1,902	1,092	1.88	2.30	1.32
	1,527	2,410	2,820	1,524	1.48	1.74	0.94

TABLE LXIII—*Incandescence of the oxides of præsodymium and neodymium*

Substance	Temp. °C.	I_0			I_0/I_{bb}		
		Red	Green	Blue	Red	Green	Blue
Pr_2O_3.....	665	0.000051	.....	.....	0.394	.....	.....
	735	.00123	.0308	.0254	1.00	2.49	2.00
	837	.0308	.0468	.0468	1.25	1.91	1.91
	960	.537	1.76	2.40	1.28	4.20	5.73
	1,037	3.03	7.08	6.22	1.55	3.63	3.19
	1,097	11.5	17.1	8.04	1.94	2.88	1.35
	1,145	26.6	31.6	11.5	2.01	2.39	.870
	1,190	50.4	53.0	43.9	1.90	1.99	1.65
	1,228	85.1	87.7	52.7	1.86	1.92	1.15
	1,263	123	132	51.2	1.61	1.72	.667
	1,294	157	175	52.7	1.35	1.51	.456
	1,328	181	221	71.1	1.00	1.24	.399
	1,394	302	361	126	.744	.929	.324
	1,462	525	659	146	.643	.796	.176
	1,527	877	1,047	367	.541	.646	.135
Nd_2O_3.....	735	.00243	.00881	.....	1.94	7.00	.....
	967	.0871	.204	.348	.152	.417	.712
	1,010	1.12	1.12	1.42	1.00	1.00	1.26

TABLE LXIV—*Incandescence of erbium oxide and cerium oxide*

Substance	Temp. °C.	I_0			I_0/I_{bb}		
		Red	Green	Blue	Red	Green	Blue
ErO.....	665	0.000032	0.00136	0.00945	0.250	10.6	68.4
	735	.00026	.00278	.0172	.214	2.25	13.9
	837	.00679	.0389	.....	.277	1.58	4.37
	960	.543	1.07	.....	1.29	2.55	3.83
	1,037	2.52	6.61	7.00	1.31	3.39	3.89
	1,097	6.55	14.5	21.4	1.22	2.45	3.61
	1,190	29.9	58.0	76.7	1.12	2.07	2.88
	1,263	130.4	310	207	1.17	2.74	2.69
	1,328	440	871	275	2.47	4.89	1.54
	1,394	725	1,298	745	1.86	3.33	1.55
	1,462	1,148	1,730	575	1.38	2.09	.695
	1,527	1,820	1,413	917	1.12	.870	.565
CeO.....	702	.0040	.0017	.....	8.95	4.72	.....
	735	.0349	.0403	.....	28.3	32.6	.....
	837	.692	1.21	.370	28.2	49.5	15.2
	960	4.92	6.53	3.02	17.7	15.6	7.21
	1,037	13.9	15.3	6.03	7.12	7.85	3.09
	1,097	28.3	21.4	15.1	4.78	3.63	2.55
	1,145	69.5	53.2	25.4	5.25	4.02	1.91
	1,190	133	133	11.7	5.02	5.02	0.44
	1,263	334	304	11.1	4.34	3.95	.144
	1,328	596	519	25.4	3.34	2.91	.142
	1,394	653	695	87.9	1.58	1.69	.227
	1,462	783	887	113	.950	1.07	.136
	1,527	1,319	1,309	423	.813	.684	.260
	1,580	3,304	1,514	656	1.23	.563	.244

IV. ERBIUM OXIDE

[Based on experiments of W. G. Mallory.]

This substance, under our present method of treatment, exhibits a modified blue glow (fig. 148) and the two outbursts at higher temperatures, just above 1000° and just above 1300° (fig. 149). On account of its banded emission spectrum it had previously been selected for study, in the Physical Laboratory of Cornell University, by the late W. G. Mallory,[1] and as his methods were in nearly every respect different from those of the present authors, it is of consider-

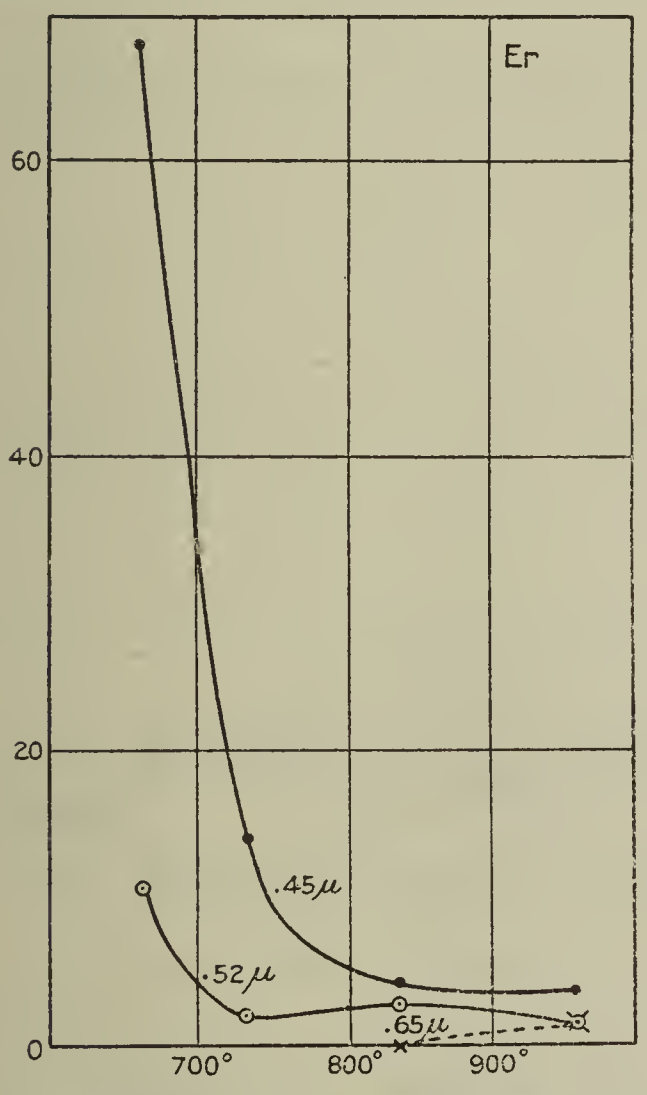


FIG. 148—The modified blue glow of erbium oxide

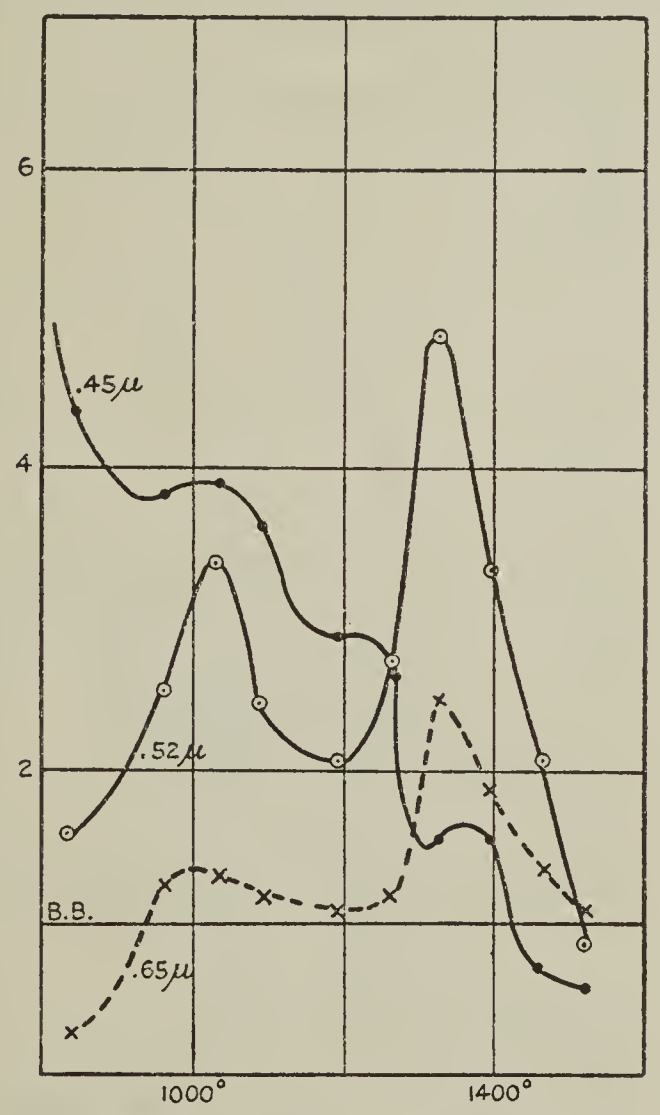


FIG. 149—The luminescence of erbium oxide at 1000°

able interest to see in how far the results of the two investigations are in agreement.

(1) *The emission spectrum not a flame spectrum*—Some erbium powder was placed upon a small piece of quartz and heated in the Bunsen flame, directly opposite the middle of the slit of a spectrometer. Sodium in the flame caused a yellow line to appear the entire length of the slit. The erbium spectrum did not extend above the solid; there was nothing like its spectrum coming from the gas immediately above the solid. This indicated that the emission was from the solid and not from the vapor near the solid.

(2) *Identity of emission from the oxide and from a phosphate bead*—There has been some difference of opinion as to whether the

[1] W. G. Mallory. Phys. Rev. (2), XIV, 54, 1919.

emission is the same from the oxide as from the phosphate. To determine this, a small portion of powdered oxide was intensely heated in the oxy-hydrogen flame and finally fused down into a cream-colored bead, without the use of any flux. This bead was mounted before the slit of the collimator and immediately above it another sample, in which sirupy phosphorus pentoxide had been used as a flux. The two specimens were in the same flame and seen at the same time, one above the other. The two spectra were identical; the red band appeared in the same place and in the same manner. The green lines appeared identical in the two spectra.

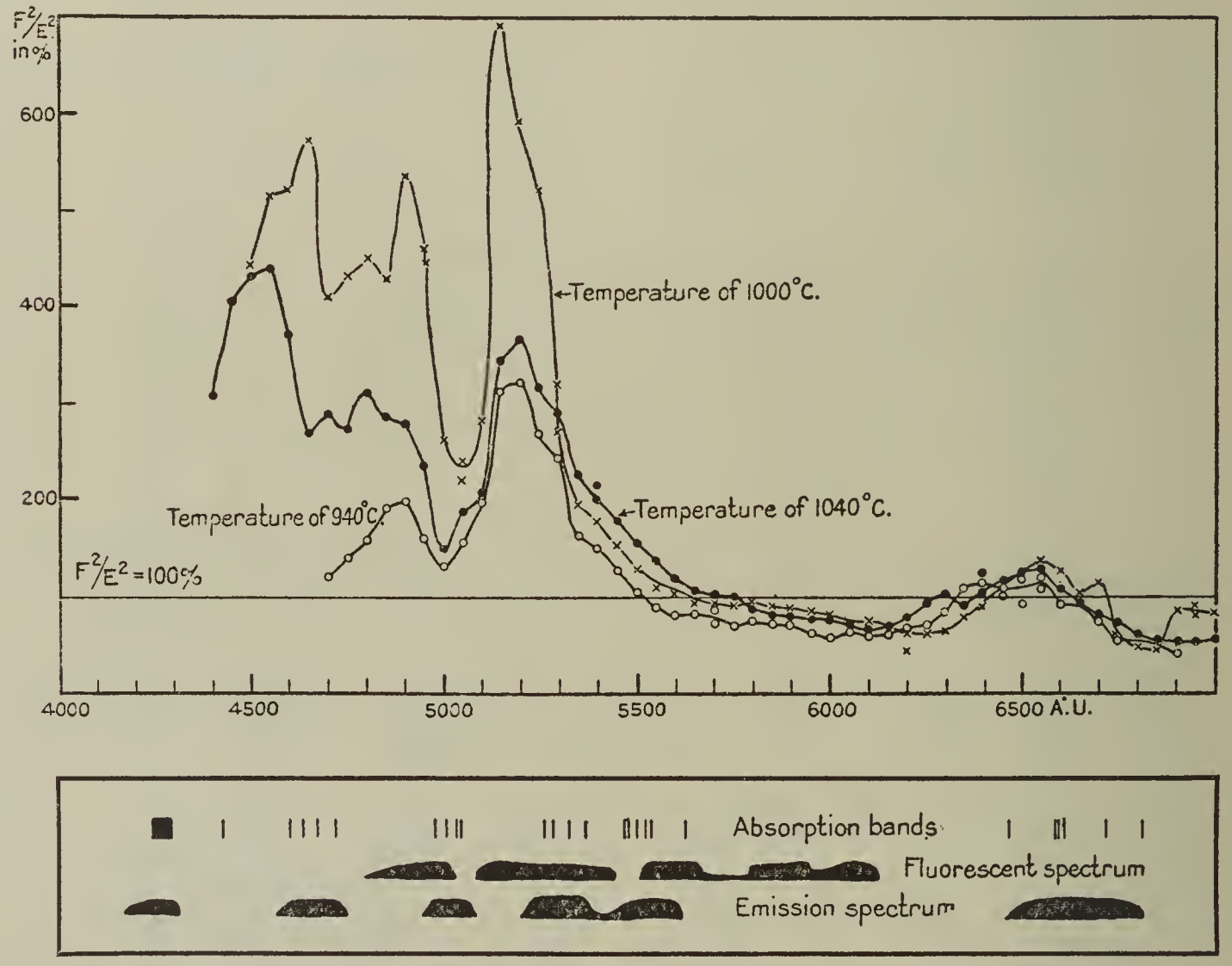


FIG. 150—Emission spectra of erbium oxide at various temperatures

(3) *Relation between emission and absorption*—It has been long recognized that there is a very close agreement in both the intensities of the emission and absorption bands. J. A. Anderson,[1] in the summary of his investigations, concluded that the emission is due to the oxide itself and that it corresponds exactly to its absorption at the same temperature. The absorption of the solid changes with temperature, the change consisting in a widening of the bands, and, in some cases, in a shift toward the red, with increase of temperature.

In the case of the oxide now under consideration the absorption

[1] J. A. Anderson. Astrophysical Jour., XXVI, 93, 1907.

bands at room temperature and the emission bands during incandescence were located visually with a spectrometer. To obtain the absorption spectrum, the fused oxide was placed before the slit of the instrument and the light of a carbon arc focused on it. As will be seen from table LXV and from the spectrum map at the bottom of figure 150, the absorption bands occur in six groups, each group corresponding approximately in position to one of the broader emission bands. The single band at 0.436μ may be the only visible member of still another group which may coincide with a feeble emission band which escaped notice.

TABLE LXV—*Absorption bands at +20° and emission bands at 1,000° observed in a specimen of commercial erbium oxide*

Group	Absorption		Emission	Group	Absorption		Emission
	μ	$1/\mu\times10^3$	μ		μ	$1/\mu\times10^3$	μ
1 (unresolved)..	0.4180 to .4223	2,392 to 2,368	0.4100 to .4250	4.....	0.5198 .5222 .5260 .5306	1,924 1,915 1,901 1,885	0.5135 to .5360
.....	.4361	2,293	.....	5.....	.5407 .5417	1,849 1,846	.5360
2.....	.4534 .4571 .4611 .4655	2,206 2,188 2,169 2,148	.4500 to .4685		.5438 .5461 .5474 .5562	1,839 1,831 1,827 1,798	to .5555
3.....	.4916 .4936 .4971 .4978	2,035 2,026 2,010 2,005	.4885 to .5015	6.....	.6400 .6521 .6532 .6551 .6656 .6751	1,562 1,534 1,531 1,526 1,502 1,481	.6400 to .6750

(4) *Fluorescence and emission*—The oxide under investigation was excited to fluorescence by cathode rays in a vacuum-tube. The spectrum, as had been noted by earlier students of the rare earths, was distinctly different from the spectrum obtained when the specimen was heated to incandescence. A broad red band began at wave-length 0.6065μ and merged into a bright yellow band at 0.5880 which extended to 0.5730. A green band began at 0.5605 and ended at 0.545. A dark space followed, and then another green band between 0.538 and 0.502. There was brightness again, beginning at about 0.495, but this gradually became less intense and ended at about 0.473. These broad bands are likewise indicated in figure 150 for convenience of comparison with the regions of emission and absorption. Since in this case the erbium oxide presumably acts as the base or "diluent," the cathode fluorescence would not be expected

to be that characteristic of erbium, but of some other element present in small quantity and acting as the "activator."

(5) *Development of selective emission with increasing temperatures*—In order to get a general idea as to the growth of the emission spectrum with increasing temperatures, some of the erbium-oxide powder was placed between two plates of thin quartz. In the midst of the powder was placed one of the junctions of a thermo-couple of Pt, Pt-Rh wires. The couple was joined through the proper resistance with a Paul unipivot pyrometer, reading approximately in degrees centigrade. The appearance at different temperatures centigrade may be described as follows:

600°. A broad faint haze in the yellow-green ending rather abruptly on the side toward the blue. No red discernible.

640°. Red band clearly seen and more light in the green, but it ended as abruptly as before.

680°. Sufficient light so that the slit could be narrowed. The green bands began to stand out from the green haze, which served as a background.

770°. A faint suggestion of another band in the blue.

800°. The red continued to stand out well, although there was a faint continuous spectrum over the whole field.

930°. Two faint bands seen beyond the green. In the red was a dark portion, as though there were two bands separated from one another.

1000°. No further question about there being varying degrees of intensity in the red. The continuous spectrum was more pronounced, yet all the bands showed well.

1120°. The band appearing in the blue seemed to be of two parts, while in the violet there seemed to be a very dim band made up of three parts. At this temperature the continuous spectrum began to mask the bands.

1220°. The red band spread into a much broader band. In the extreme violet another band could be dimly seen. The boundaries of the green bands could be seen distinctly. The other bands appeared as broad patches, slightly more intense than the continuous spectrum, which had pretty completely masked them.

(6) *Emission not due to excitation by radiation of short wavelengths*—In the article by J. A. Anderson it was suggested that the simplest and best way to settle the question whether the radiation is due to the oxide itself or to a surface layer of gas formed by the action of the flame, would be to heat the oxide without using the flame. In order to make this test, and at the same time prevent the excitation of fluorescence by any ultra-violet radiation from the flame itself, a nickel box about 2 cm. in diameter and 7.5 cm. in depth

was used. This box was heated by a blast-lamp flame playing against the bottom and sides. The specimen to be examined was mounted on the end of a bent quartz rod, in such a manner that it could be quickly swung up out of the box and before the slit of the collimator. When heated in this manner the red and green bands were seen, just the same as when the specimen was heated by the flame directly. The nickel box was not white hot, and the bands persisted for several seconds after the cooling had begun, due to removal from the box. Since performing the experiment with the nickel box, specimens have been heated in the electric furnace, to be described in a subsequent paragraph, and the spectrum has been found to be the same as when heated directly by the flame. This is taken to establish that the banded emission spectrum is not due in any way to peculiar properties of the flame, but that it is a thermal effect and independent of the manner of heating.

DISTRIBUTION OF ENERGY IN THE EMISSION SPECTRUM

The main purpose of Mr. Mallory's investigation was to determine whether the emission of the bright bands exceeds that in the corresponding regions in the spectrum of a black body at the same temperature. If so, the well-known corollary of Kirchhoff's law, that no body can emit more radiation of a given wave-length than does a black body at the same temperature, is inapplicable to these highly selective radiators.

The instrument employed was a spectrophotometer designed for the study of luminescence spectra,[1] similar to that shown in figure 7, Chapter I. The comparison light which moved along the photometer track *BB* was a straight-filament 10-volt lamp. In front of the other collimator at *P* was a track at right angles to the axis of the collimator, on which ran a carrier for a small electric furnace and the erbium oxide. By moving the carriage between suitable stops either the furnace or the specimen could be brought before the slit. It was thus possible to compare the radiation from either the interior of the furnace or the oxide with the radiation from the comparison lamp, by a method of substitution. If there is a match of the two fields when the furnace is before the slit, and this match is destroyed when the oxide has replaced the furnace, there can be no doubt as to which gives the stronger radiation for that particular part of the spectrum.

Erbium-oxide powder was mounted between two thin pieces of clear fused quartz, thus presenting a matte surface to the slit. This surface was about 1 cm. long and 0.6 cm. broad at the top, with an

[1] E. L. Nichols. Proc. Am. Philos. Soc., LVI, p. 262, 1917.

average thickness of 0.15 cm. A colorless hydrogen flame played around the quartz holder. When heated, the powder would glow while the surrounding border of clear quartz would remain transparent and nearly non-luminous. A slender quartz rod, fused to the bottom of the holder, supported the arrangement. Two thermo-junctions were made out of platinum and platinum-rhodium wire which had been carefully tested and found to give no E. M. F., due to lack of homogeneity. One of these couples was used to determine the temperature of the powder, a junction being placed in the midst of the powder. One junction of the other couple was immediately in front of the partition in the middle of the electric furnace, the inner construction of which was similar to the well-known "Reichsanstalt" black body. The tube was 45 cm. in length and had an internal diameter of 3 cm. The photometer was sighted on a disk placed in the middle of the tube. A number of diaphragms in the tube served to prevent air-currents.

When heated, it was impossible to make out the boundary of the disk or the wires of the thermo-junction. Both thermo-couples were connected through switches to a Wolff potentiometer, and it was also possible to join the couples in opposition through a Sullivan galvanometer of such sensibility that a temperature of one degree centigrade was easily detected by the movement of the spot of light. Since taking the data, the junctions have been compared and found to agree within 0.00002 volt throughout the temperature range from 700° C. to 1046° C. The temperature as gotten from the potentiometer readings are probably not in error by more than two degrees at any time.

Uniformity of temperature over the surface of the oxide was tested for with a Morse thermal gage. This method, while not very delicate, was fairly conclusive so far as the detection of considerable temperature changes is concerned. In the exploration of one specimen, for example, that had been used for several runs, the indicated temperature variations were from 827° C. to 840° C., or a variation of 13°. Readings taken at different points varied no more, however, than when the successive settings were all made upon the same point. For both cases the average departure of the temperature from the mean was about 1.8 per cent.

The use of clear quartz as a mounting in these experiments is essential. When heated in the flame up to 1200° C. it remains so nearly non-luminous that its visible spectrum is of a low order of intensity. Other advantages of the quartz are that it does not soften at the high temperatures at which the experiments were carried on, and that at a high temperature it is a good conductor of heat. It is essential that the quartz be free from air-bubbles, for although the

clear quartz when heated emits little or no visible radiation, if it contains spots made up of an emulsion of quartz and air these spots emit strongly, and this is true even when the spots are at some distance from the heated portion of the tube or rod.

When making observations, the two couples were commonly joined in opposition through the galvanometer. It was possible to keep the temperatures nearly constant. No readings were taken when the two temperatures differed by as much as 10 degrees. In the case of a lesser difference the readings were not used in plotting the curves, except when the furnace temperature was the higher of the two. The furnace and the oxide were alternately placed before the slit. Three readings were made for each, at each wave-length. When working near the end of the visible spectrum it was sometimes difficult to make an exact setting, but when the shift was made it was possible to tell whether the furnace or the oxide gave a more brilliant field.

In the spectrophotometric determinations the two collimator slits were set at equal width once for all, the slit-widths being as small as the intensity of the weaker regions of the spectrum would permit. The carriage upon which the furnace and incandescent oxide were mounted was brought to the position where the light from the furnace entered the collimator. The place on the photometer bar where light from the comparison lamp matched that from the furnace was determined when the thermo-couples indicated equality of temperature between furnace and oxide. The carriage was then immediately shifted so as to bring the oxide before the slit and the position of the lamp readjusted to a match. If the balance of temperatures was still satisfactory, the readings on the photometer bar were accepted. Readings were made at intervals of 50 Ångström units.

In this method of substitution, if F is the distance on the photometer bar from the slit to the filament of the comparison lamp, when the fields are equally bright and the furnace is before the other slit, while E represents the corresponding distance, with the oxide before the slit, then F^2/E^2 gives the ratio of emission of the oxide and the black body for the temperature in question and the wave-length under observation. The results of a typical experiment, one of many, are given in table LXVI and graphically in the curves of figure 150. The measurements were made at 940°, 1000°, and 1040° C. In the curves, values of F^2/E^2, which give the relative intensities are plotted as ordinates and wave-lengths as abscissæ. The results are quite different from what was expected, it having seemed probable that the curves might approach a radiation approximately equal to that from a black body for the wave-lengths corresponding to the strong emission bands.

Below the curves showing the emission of the oxide when compared to that of the black body at the same temperature are shown the three spectra mentioned in an earlier paragraph. They were obtained from a sample of the erbium oxide prepared with a flux. The first one shows the absorption when the substance is placed before the slit and the light from a carbon arc is focussed upon it; the second shows the fluorescent spectrum when it is excited by cathode rays in a vacuum-tube; the third shows the emission spectrum when the same specimen is heated in the oxy-hydrogen flame. The close agreement of the positions of the bands in the emission and absorption spectra can easily be seen.

TABLE LXVI—*Emission of erbium oxide referred to that of a black body at the same temperature*

Wave-length	Relative Intensity			Wave-length	Relative Intensity		
	940°	1000°	1040°		940°	1000°	1040°
μ				μ			
0.4400	.....	.....	3.06	0.5750	0.70	0.85	0.98
.4450	.....	.....	4.06	.5800	.72	.92	.88
.4500	.....	4.42	4.29	.5850	.70	.90	.84
.4550	.....	5.14	4.39	.5900	.70	.82	.80
.4600	.....	5.20	3.68	.5950	.62	.82	.80
.4650	.....	5.72	2.48	.6000	.58	.80	.78
.4700	1.20	4.08	2.86	.6050	.62	.72	.70
.4750	1.40	4.30	2.74	.6100	.59	.73	.65
.4800	1.55	4.50	3.11	.6150	.60	.70	.70
.4850	1.92	4.28	2.85	.6200	.62	.62	.79
.4900	2.00	5.35	2.79	.6250	.65	.71	.94
.4950	1.60	4.50	2.35	.6300	.82	.64	1.00
.5000	1.34	2.60	1.48	.6350	1.05	.82	.92
.5050	1.58	2.30	1.92	.6400	1.12	.96	1.08
.5100	2.10	2.80	2.12	.6450	1.08	1.15	1.18
.5150	3.14	6.88	3.46	.6500	1.12	1.26	1.22
.5200	3.20	5.90	3.65	.6550	1.12	1.36	1.28
.5250	2.68	5.90	3.19	.6600	.90	1.28	1.06
.5300	2.41	2.68	2.68	.6650	.92	1.02	.92
.5350	1.62	1.94	2.24	.6700	.72	1.14	.75
.5400	1.51	1.79	2.04	.6750	.57	.62	.72
.5450	1.26	1.52	1.79	.6800	.52	.56	.62
.5500	1.04	1.22	1.44	.6850	.48	.44	.58
.5550	.88	1.09	1.39	.6900	.42	.90	.57
.5600	.80	1.02	1.18	.6950	.....	.87	.56
.5650	.80	.95	1.05	.7000	.....	.84	.58
.5700	.75	.85	1.00				

The range of temperatures employed in the spectrophotometric examination was so small, when we consider the necessarily somewhat uncertain temperature control in the use of the hydrogen flame, that relative positions of the curves for 1000° and 1040° may perhaps be open to question. The evidence, however, seems strongly to favor the existence of a critical temperature at about 1000°.

To check the foregoing temperature determinations, the following

modification of mounting was tried: A piece of clear quartz tubing, 3 mm. internal diameter, was sealed at the lower end. Powder was tamped into the tube to a depth of 2.5 cm. The thermo-junction was placed in the midst of the powder, opposite the middle of the slit. This tube was rotated about a vertical axis, thus heating the powder from all sides. Small quartz tubes inclosed the lead wires which at the upper end made contact with two rings of mercury, and through these rings the connection was made to the potentiometer and galvanometer, as before. The flame in this case rises about the tube containing the wires, which are heated to incandescence for 2 or 3 cm. above the top of the powder. With this arrangement there is no doubt as to which of the two sources gives the more intense radiation. Without making complete runs with this set-up, an examination of the spectrum at those wave-lengths where the radiation is most intense has shown the effect to be of the same order of magnitude as indicated in the curves.

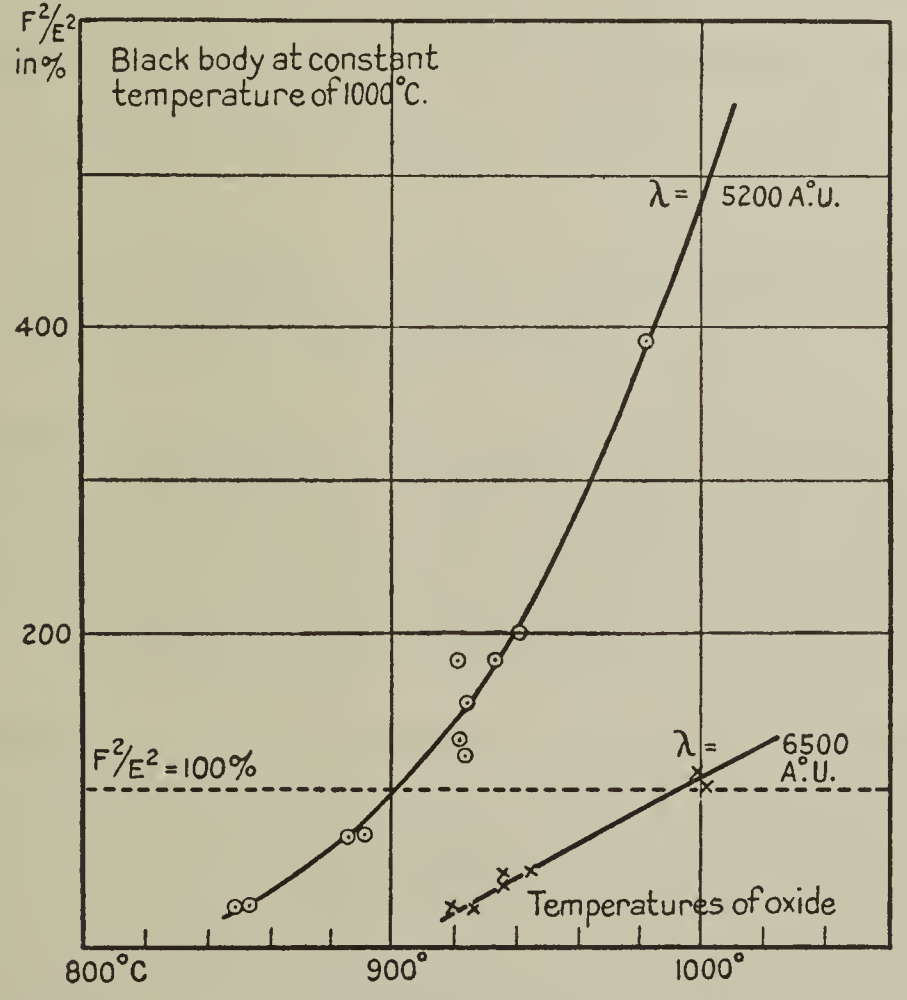


FIG. 151—Ratio of intensities of erbium oxide radiation to black-body radiation

A further check was obtained by determining the temperature at which the emission bands of the oxide would give the same radiation as the black body at 1000° C. In this experiment the furnace was kept at that temperature and readings were taken for several temperatures of the oxide. Observations were made in only two portions of the spectrum—in the red at wave-length 0.6500μ and in the green at 0.5200μ.

The results, which are plotted in figure 151, do not correspond quantitatively in all respects with the spectrophotometric determinations. That is because we happen to have to do in this experiment with a less intense selective radiator. Preparations of erbium oxide vary very widely in this respect. The radiating power, for example, is greatly lessened when the oxide is fused down in the electric arc. The bands are visible in such cases, but at no wavelength does the radiation equal that from the furnace at the same temperature. Although the sample used in the test just described was obviously less active than that previously employed in the exploration of the spectrum, the green band attained at 900° a brightness equal to the corresponding region in the spectrum of the black body at 1000° and at 980° was four times as intense. The red band at 1000°, however, barely exceeded the black-body radiation at that temperature.

SUMMARY

(*a*) As a result of this investigation, it seems certain that the peculiar banded emission of erbium oxide is due to the oxide itself and requires nothing more than a sufficiently high temperature to bring it out. The manner of obtaining this temperature seems to be of no importance.

(*b*) The emission bands at 1000°, especially in the green, are found to radiate much more strongly than a black body at the same temperature.

(*c*) The temperature at which the emission of the green bands equals that of a black body at 1000° is about 900°. This difference of temperature is much greater than that which could possibly have existed in the comparisons which were made under conditions where approximate equality of temperature was indicated.

V. SECONDARY FEATURES INDICATIVE OF LUMINESCENCE[1]

(1) *Fatigue*—The first heating of the oxides studied in this chapter to moderate incandescence was frequently found to produce a brightness greatly in excess of that existing after a given temperature had been maintained for some time. The decay, as was to be expected, was very rapid at first and had a diminishing rate. No attempt has been made as yet to determine the curve of decay. A few estimates of the initial brightness of magnesium oxide at a temperature of 1220° gave the following result (observations were for 0.45μ): $I_0=2690$; $I_{bb}=41.3$; $I_0/I_{bb}=65.3$. The usual value at this temperature for several minutes after ignition was less than unity (see fig. 152). The above readings were made about 0.3 second after

[1] Nichols and Howes. Phys. Rev. XIX, 314, 1922.

ignition and are doubtless too late for the actual maximum. This fatigue has long been known in the case of lime cylinders against which an oxyhydrogen flame impinges, and decay curves were made many years ago.[1]

Probably the limiting value for initial brightness is obtained when a metal like magnesium is burned. W. H. Pickering,[2] long before the general laws of radiation had been developed, estimated the temperatures corresponding to the spectral distribution of the light from the magnesium flame at 4900° C. It is now easy to check his value, which was based upon a purely empirical relation between the ratio of red and blue in the spectrum and the temperature, by apply-

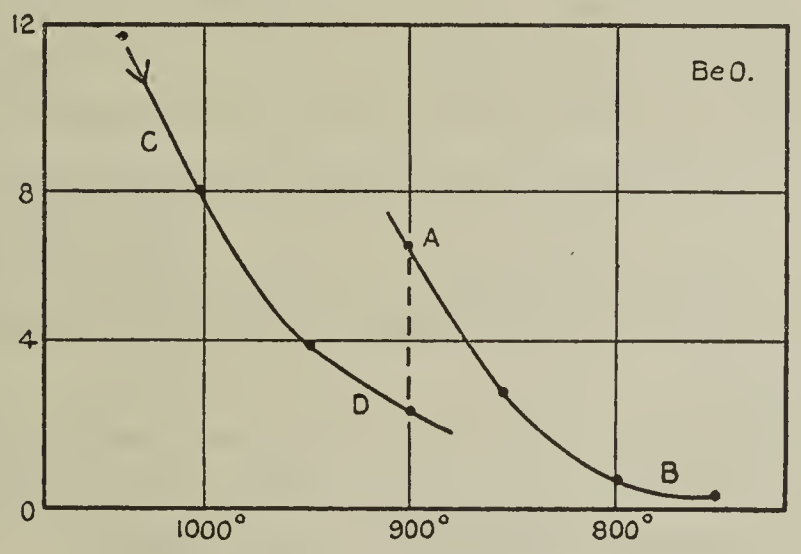


FIG. 152—Fatigue due to previous heating of beryllium oxide

ing the distribution law to the spectrum of this flame. The result gives about 5000° C., and since the actual temperature of the flame, as studied by F. J. Rogers,[3] can not be above 2000°, this means that 98 per cent or more of the light must be ascribed to luminescence.[4]

(2) *Effects of heat treatment*—As in the preparation of phosphorescent substances for excitation by light or by cathode rays, so here the effects of previous heat treatment are varied and complicated.

In some cases the previous heating of an oxide to full incandescence seems to be essential to the blue glow and to other luminescent outbursts belonging to the lower stages (below 1000°). Sometimes, however, heating to moderate temperatures reduces the glow. A sample of beryllium oxide not previously ignited was heated in the H-O flame to about 1000° and after a fairly stable state had been reached was allowed to cool, stepwise, by gradually reducing the flame. In this way the upper curve (*AB*) in figure 152 was obtained. The temperature was then increased to about 1300°. The lower curve (*CD*) indicates the brightness on cooling after this treatment.

Heating to incipient fusion, *i. e.*, until the surface of the oxide

[1] Nichols and Crehore. Phys. Rev. (1), II, p. 161, 1894.
[2] W. H. Pickering. Proc. Am. Acad. Arts and Sciences, 1879-80, p. 236.
[3] F. J. Rogers. Am. Jour. of Science, XLIII, p. 301, 1892.
[4] Nichols. Trans. Ill. Eng. Soc., XVI, p. 331, 1921.

became mobile as observed with the pyrometer, had in one instance a more striking result. A sample of aluminum oxide which showed the blue glow, and which on further heating step by step developed the usual outbursts at 1000° to 1100° and 1300° to 1500°, showed signs of fusion. On cooling stepwise in the flame the outburst at 1300° to 1500° was repeated, but of the luminescence at lower temperatures all but a trace was gone. The intensity at 735° as viewed through the blue screen was now $I_0/I_{bb}=1.02$ instead of the previous value of 67.3.

(3) *Influence of the mode of heating*—The type of luminescence now under consideration, unlike the luminescence by flame excitation described in a previous section, is not confined to substances exposed to the action of the hydrogen flame. It is, for example, possible to see the blue glow when beryllium oxide is heated in a crucible, or when zinc oxide or other oxides are electrically heated on a strip of platinum foil. The effect is, however, much more intense when the flame is used, and the brightness is greatly affected by changes in the supply of oxygen so slight that the actual temperature, as indicated by the radiation from the black surface, is not appreciably modified. The following observations upon magnesium oxide, using adjustments of hydrogen and oxygen such as to maintain a constant temperature, may serve to illustrate this point:

MgO. Temperature 1220°, $I_{bb}=41.3$;
With excess of hydrogen, $I_0=57.0$; $I_0/I_{bb}=1.38$;
With excess of oxygen, $I_0=151$; $I_0/I_{bb}=3.66$.

The general luminescent activity of the oxide was somewhat greater than in the foregoing experiment on fatigue.

It was noted in the course of these trials that the sensitiveness to oxygen seemed to differ with the various oxides and for a given oxide was much greater at some temperatures than at others. This presumably depends on whether the observation is made at a temperature corresponding to one of the outbursts of luminescence. This is a point not yet definitely established by systematic experiments with several different oxides. It was noted, however, in the course of our measurements with præsodymium oxide, that this substance was exceedingly sensitive to the slightest changes in the supply of oxygen at temperatures around 1000°. Above 1300°, where there is little but temperature radiation in evidence, this sensitiveness had disappeared.

VI. EFFECTS OF FREE OXYGEN[1]

Throughout the experiments on incandescent oxides, the influence of the relative paucity or abundance of free oxygen was clearly a factor of great importance. In the case of *titanium oxide,* the amount

[1] E. L. Nichols. Phys. Rev. XXII, p. 420, 1925.

present determines the character of the light emitted to an extraordinary degree. In fact, at any temperature between the red heat and 1200° the emitted light from a mass of the oxide upon which an oxy-hydrogen jet impinges may be changed from a deep red to a blue by a very slight adjustment of the gases in the flame. We have, indeed, two distinct phases of incandescence, and these have been compared throughout a range of over 500°. They may be briefly characterized as follows:

Phase R (oxygen meager) is distinguished by an outcropping of luminescence which reaches a sharply defined maximum just below 1000° and which affects the whole visible spectrum. The red of the spectrum is relatively somewhat stronger at all temperatures between 800° and 1050°. In a measurement made at the crest of the curve the red (0.65μ) was 11.0 times, and the blue (0.45μ) 9.8 times as bright as the corresponding regions in the spectrum of a black body at the same temperature.

TABLE LXVII—*Luminescence of incandescent titanium oxide (TiO_2)*

	Temp. °C.	I_{bb}	I_o			I_o/I_{bb}		
			Red, 0.65μ	Green, 0.52μ	Blue, 0.45μ	Red, 0.65μ	Green, 0.52μ	Blue, 0.45μ
Phase O, oxygen in excess.....	692	0.000255	0.00107	0.0142	0.0451	3.63	48.3	153
	773	.00366	.0338	.169	.0574	8.79	43.9	149
	882	.0592	.530	1.53	7.15	7.82	22.5	105
	970	.4360	1.53	8.30	10.6	3.05	16.6	21.3
	1,044	2.055	7.10	13.2	13.8	3.01	5.62	5.86
	1,110	6.170	13.5	16.6	20.5	2.70	3.18	3.18
	1,166	15.61	22.6	29.9	30.8	1.27	1.71	1.71
	1,219	34.20	46.2	53.7	52.5	1.18	1.37	1.37
	1,268	71.70	83.1	83.1	83.1	1.00	1.00	1.00
Phase R, hydrogen in excess...	692	0.000255	0.000196	0.000294	0.000294	0.668	1.00	1.00
	773	.00366	.00562	.00638	.00638	1.426	1.656	1.66
	882	.0592	.342	.281	.281	5.05	4.15	4.15
	970	.4360	5.62	4.78	4.78	11.2	9.55	9.55
	1,044	2.055	16.4	16.4	16.4	6.96	6.96	6.96
	1,110	6.170	19.3	23.6	23.6	2.99	3.67	3.67
	1,166	15.61	19.3	19.3	26.8	1.25	1.25	1.51
	1,219	34.20	38.0	38.0	44.6	1.111	1.111	1.14
	1,268	71.70	71.7	71.7	71.7	1.00	1.00	1.00

Phase O (oxygen in excess) is a modified "blue glow." At 700° the brightness in the blue (0.45μ) was found to be over 150 times that of the black body, in the green (0.52μ) 48 times, and in the red (0.65μ) 8 times. The effect differs from the normal "blue glow" of Al_2O_3, BeO, CaO, etc., in that the maximum of relative intensity is within the incandescent range, instead of at some lower temperature, and in that the luminescence extends to the green and red of the

spectrum.[1] Above 1200° all excess radiation disappears and the spectrum coincides with that of a black body, both in distribution and brightness. These values appear more definitely in table LXVII, in which the brightness, in terms of that of a black body at 1000° C., of three regions of the spectrum (red, green, and blue) is given for both phases of incandescence, and also the ratio I_0/I_{bb} of these intensities to those of the corresponding regions in the spectrum of a black body of the same temperature.

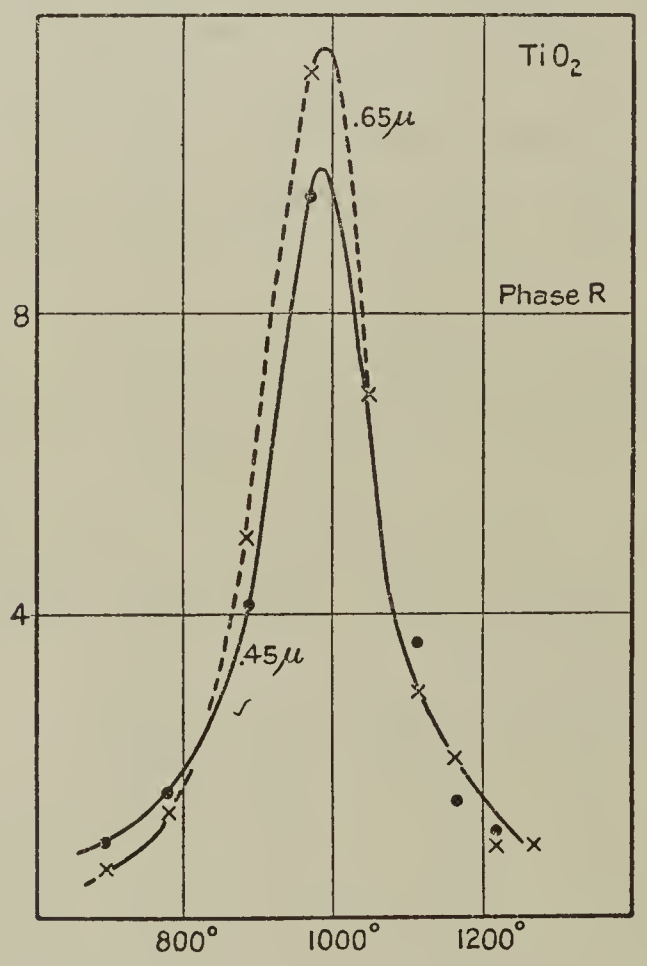


FIG. 153—Luminescence of TiO_2 (phase R)

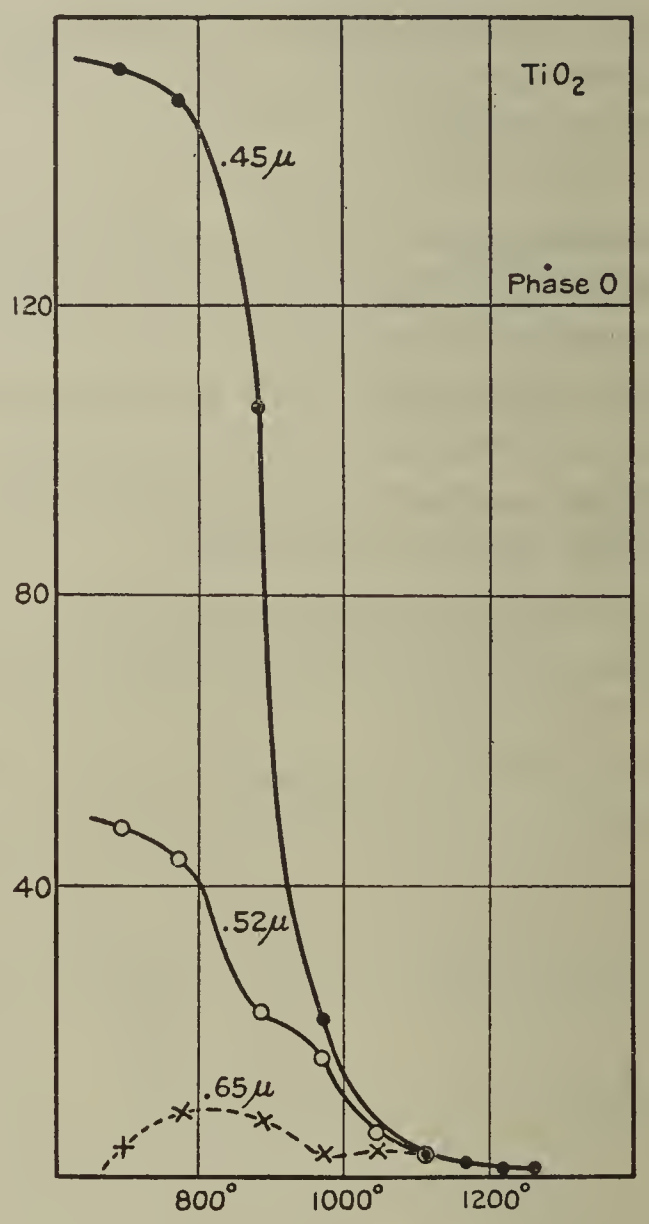


FIG. 154—Phase O of TiO_2 (oxygen in excess)

How well defined the outcropping of luminescence is in *Phase R* and how sharp its crest at 985° C. may be seen in figure 153. The glow which characterizes *Phase O* is illustrated in figure 154. The maximum value of I_0/I_{bb} is evidently to be found not far below 700° C. The relative brightness of the green is more than one-fourth that of the blue, while the red glows more strongly than the corresponding black body throughout the whole of the range of incandescence. It is for these reasons that the effect in *Phase O* is described as a *modified* blue glow. The remarkable fact is that in both phases the radiation from this oxide throughout the visible spectrum is *in excess* of black-body radiation for the whole range of temperatures from the threshold of visibility to 1200° C.

[1] Nichols and Howes. Jour. Opt. Soc. Am., VI, 42, 1921.

Columbium oxide[1]—This white and highly refractory oxide likewise exhibits in the character of its visible radiation at the lower stages of incandescence the remarkable effects of free oxygen. When a fragment a few millimeters in diameter is gradually inserted from the side into the outer layers of a hydrogen flame, instead of becoming "red hot" it glows with a pale greenish-blue color. Pushed farther into the flame, the color of the incandescent fragment changes abruptly to a deep red.

The contrast is a most striking one and the transition may readily be shown to depend on the position of the oxide within the flame rather than upon any change of temperature. These two types of radiation, which, in conformity with the foregoing study of somewhat similar conditions in the incandescence of titanium oxide, we shall call respectively *Phase O* and *Phase R,* are mutually and instantly interchangeable. So sharp is the boundary between the portions of the flame where they occur that it is easy to move the bit of oxide into a position where the inner part, lying nearer to the axis of the flame, is red, and the outer, in the oxidizing layer, is green-blue. If, now, the piece of oxide be made to oscillate at right angles to the axis of the flame, this boundary will be seen to be fixed with reference to the flame. There is no perceptible lag, such as would be easily observable if the change depended upon alternate heating or cooling of the oxide.

SPECTROPHOTOMETRY OF THE VISIBLE RADIATION

Through a spectroscope of low dispersion the spectra of both phases are seen to be continuous, but the appearance of that of *phase O* suggests a group of very broad, nearly submerged bands covering the entire range of the visible region. For the comparison of these spectra the following scheme was adopted:

Across the outer surface of the base of an alundum crucible a shallow depression was cut about 0.05 cm. deep and 1.0 cm. in width. This served as a holder for a thin layer of the oxide which could be pressed into the channel in powdered form, completely filling it, with the smooth face of the layer flush with the alundum surface on either side. Thus mounted, it could be raised into a vertical plane and heated by means of the hydrogen flame without breaking down. With a camel's hair brush half of the surface of the oxide was moistened with a solution of uranyl chloride, leaving a sharp dividing line, *LL,* as in figure 155. After heating, the moistened region remained impregnated with uranium oxide, which, as in our previous work, imparted to it the radiating properties of a very nearly perfect black body.

[1] E. L. Nichols. Phys. Rev., XXV, p. 376, 1925.

When a flame of hydrogen, *HH,* from a small vertical jet, *J,* was brought up until its outer layers were in contact with the layer of oxide, the region *B,* to the left of the median line, became red hot, while the corresponding region, *W,* to the right, assumed the radiating condition known as *phase O.* An image of the contiguous fields of glowing material was then sharply focussed upon one collimator slit of a large Hilger spectro-photometer with the line *LL* parallel to the slit. By turning a sheet of plate glass, *G* (fig. 156), in the path of the beam of light, the image of *BW* could be shifted to the right or left, so that the portion corresponding to *B* alone or to *W* alone would fall upon the slit *S.* Thus, any desired wave-length of the spectrum of the light from *B* or *W* could be compared with the corresponding wave-length of the comparison lamp mounted, in the manner described in the account of our spectrophotometric work, on a photometer bar before the other slit of the spectrophotometer. The comparison source was a tungsten filament of low voltage maintained by a storage battery at approximately 2000° C. By turning *G* through a predetermined angle, the field could be shifted back and forth between *B* and *W* at will, and thus, by the method of substitution, the relation of these spectra to one another could be readily determined.

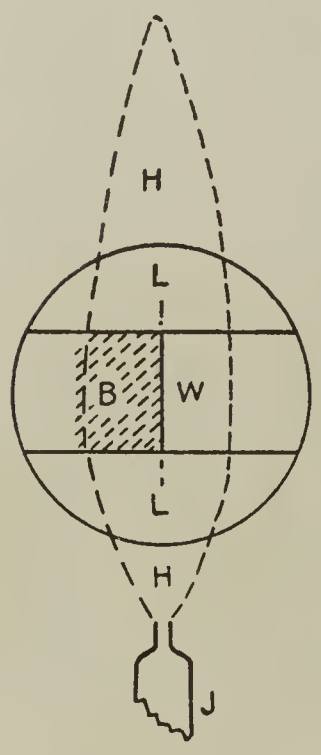


FIG. 155—Presentation of the oxide to the hydrogen flame

By moving the hydrogen flame a trifle nearer to the base of the crucible and thus converting *phase O* of the radiation of the Cb_2O_5 into *phase R,* a similar set of observations gave the relations between the spectra of this phase and the spectrum of the comparison lamp or of the uranium oxide respectively.

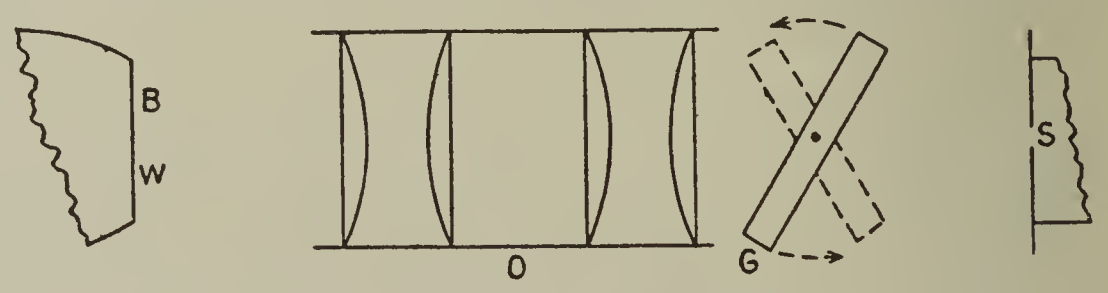


FIG. 156—The optical system

These measurements give directly the composition of the visible radiation from the glowing oxides in terms of the composition of the light from the comparison lamp.

In table LXVIII, as already stated, I_0 is the brightest of the glowing columbium oxide (*phase O*) in terms of that of the corresponding region in the spectrum of the comparison lamp. The conditions of the measurements were such that the two spectra were very nearly of equal brightness in the yellow (at 0.5890μ). Similarly, $I_{bb'}$ is the brightness, under the same conditions of comparison, of the

glowing uranium oxide. To make the values of I_0 and I_{bb} as nearly as possible strictly comparable, measurements of the two were made alternately throughout the spectrum.

TABLE LXVIII—*Distribution of intensities in the spectrum of Cb_2O_5 (phase O)*

μ	I_0	I_{bb}	I_0/I_{bb}	μ	I_0	I_{bb}	I_0/I_{bb}
0.4590	0.0930	0.0240	3.88	0.5771	1.320	0.2834	4.76
.4675	.1551	.0266	5.83	.6018	.9766	.4852	2.01
.4793	.2488	.0310	8.02	.6298	1.008	.5333	1.89
.4918	.2825	.0363	7.79	.6620	.8503	.8547	.996
.5052	.2644	.0472	5.99	.6765	1.468	1.294	1.134
.5175	.2644	.0643	4.13	.6924	1.276	1.693	.754
.5372	.6645	.1480	4.49	.7007	1.562	1.762	.886
.5557	1.457	.2635	5.53	.....	.....	.....	.....

In figure 157, I_0 is plotted as a function of the wave-length and the corresponding intensity of the spectrum of the comparison lamp is

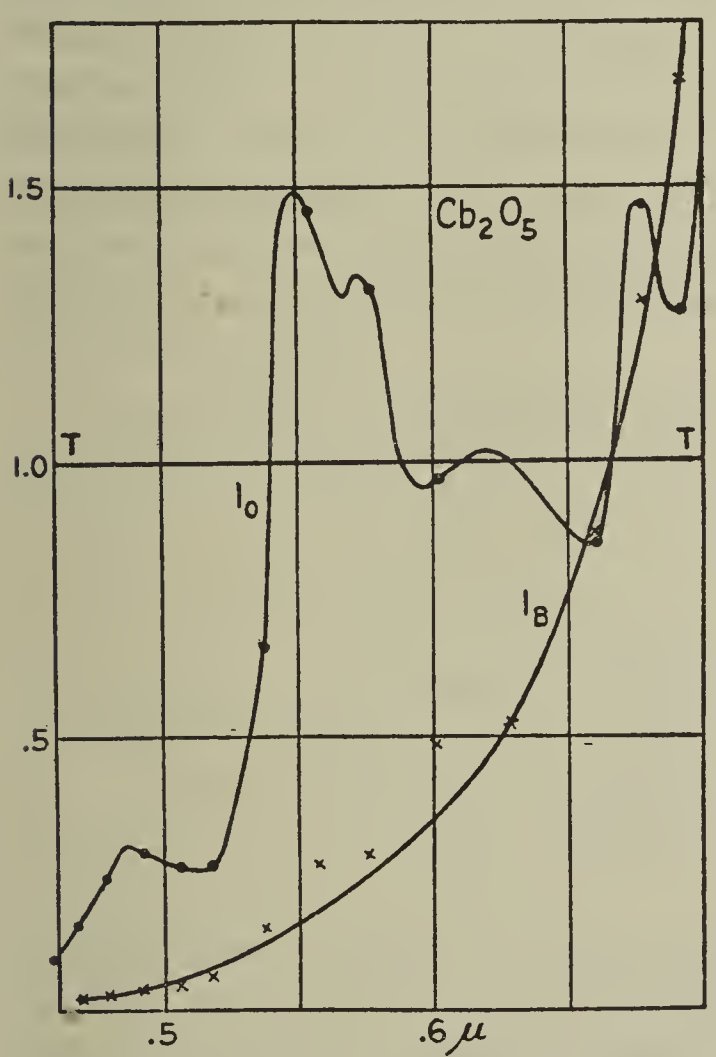


FIG. 157—Intensity distribution I_0 of spectrum of Cb_2O_5, taking the comparison spectrum as unity, *TT*

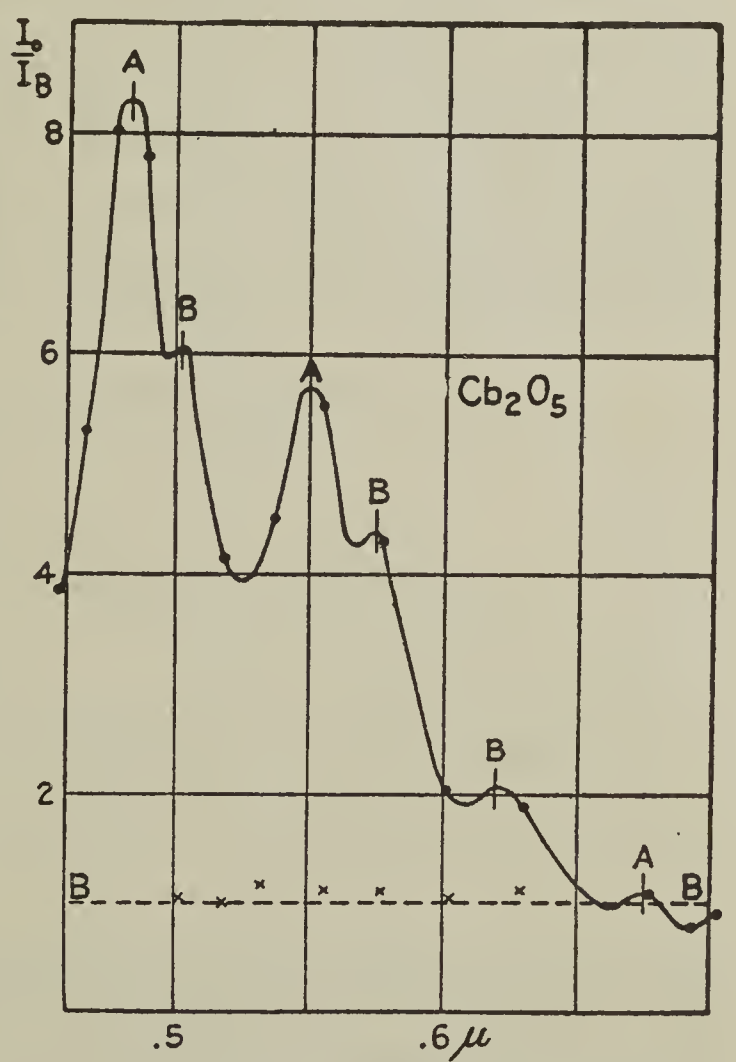


FIG. 158—Intensity distribution of spectrum of Cb_2O_5 referred to that of a black body taken as unity, *BB*

represented by the horizontal line *TT* having the ordinate unity. Clearly, the spectrum of Cb_2O_5 under conditions which give radiation of *phase O* consists of several rather broad overlapping bands. Uranium oxide, on the contrary, at the same temperature, *i.e.*, at 820° C., as determined by the optical pyrometer, shows no indications

of a banded spectrum. The curve I_{bb} (also given in fig. 161) is of the character which one would expect to obtain for a non-selective radiator at the temperature in question.

Knowing the distribution of intensities in the spectrum of the comparison lamp, the values of I_0 might readily be expressed in terms of relative energy, but it is more interesting for our present purpose to compare the radiation of the glowing columbium oxide with that of a black body at the same temperature. This comparison is afforded by the ratio I_0/I_{bb} for the various regions of the spectrum, and graphically in figure 158, where I_{bb} is represented by the horizontal line *BB* of ordinate unity. The curve for I_0/I_{bb} in this diagram brings out the crests of the overlapping bands more definitely than does the corresponding curve in figure 157. The resolution is not sufficient to bring out the finer structure of the spectrum, but six crests may be quite closely located.

In the study of calcium oxide[1] and of certain sulphides when excited to luminescence by the hydrogen flame already described, we found their spectra to be made up of overlapping bands equidistant as to frequency and coincident with the bands of the same substance when excited by cathode rays.[2] T. Tanaka,[3] in the exhaustive investigation of the spectra of cathodo-luminescent substances, described in Chapter III, has established a definite relation between the frequency-interval between bands and the atomic weight of the activating element. A consideration of the frequency relations of the crests in figure 158 is therefore not without interest. Tanaka's interval for columbium would be very close to 21 and an inspection of the location of the bands in the spectrum now under consideration shows that they may in fact be arranged in two sets such that the distance, measured in frequency units, between neighboring mem-

TABLE LXIX—*Frequency relations of the bands of phase O*

	Set A			Set B	
	$1/\mu \times 10^3$	Difference		$1/\mu \times 10^3$	Difference
0.4831	2,070		0.5020	1,992	
		252=21×12			252=21×12
.5500	1,818		.5747	1,740	
		336=21×16			126=21× 6
.6748	1,482		.6196	1,614	

[1] H. L. Howes. Phys. Rev. (2), XVII, p. 469 (1921); see also Chapter VIII.
[2] Nichols, Howes and Wilber. Phys. Rev. (2), XII, p. 351 (1918); see also Chapter VIII.
[3] Tanaka. Jour. Opt. Soc. Am., VII, p. 287, 1924.

bers of a set is an even multiple of Tanaka's interval. Calling these sets *A* and *B*, we find the relations shown in table LXIX. It is believed that the crests recorded in the table represent groups of bands rather than single bands.

PHASE O; A LUMINESCENT EFFECT

That the visible radiation indicated graphically in figure 158 is partly at least to be ascribed to luminescence is obvious when we consider that all intensities above the horizontal line *BB*, or one very near to that, are in excess of the black-body intensities for the various wave-lengths and at the given temperatures. That the portion of the area under the curve which is due to temperature radiation must be much smaller than that which would correspond to a black body becomes obvious when we flood the radiating surface with white light strong enough to quench the incandescence. It is then seen that we have to do with an oxide *nearly white*, and therefore capable of relatively feeble radiation in accordance with the Kirchhoff relation.

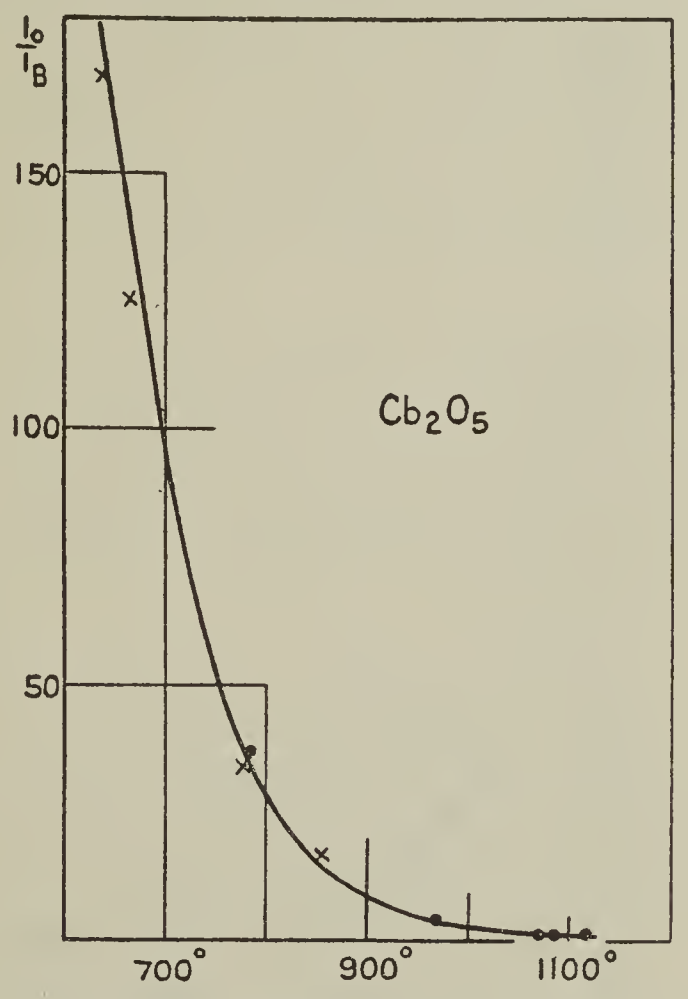


FIG 159—Ratio of brightness to that of a black body, as a function of temperature

In addition to the above criterion there are the following characteristics which suggest luminescence:

(*a*) *The spectral structure*—This, which, as has already been pointed out, consists of overlapping bands occurring in sets the members of which have a constant-frequency interval, is characteristic of all luminescence spectra.

(*b*) *The ratio of brightness to that of a black body* of the same temperature diminishes rapidly with rising temperature and approaches unity at temperatures above 1000°. The change of the ratio of I_0/I_{bb} with the temperature in figure 159, in which observations grouped along the logarithmic curve indicate the ratios obtained in two overlapping runs, one for the lower, designated by the mark X and for the higher ranges by O.

The curve in figure 159 is similar to those found for the *blue glow*[1] of such oxides as CaO, MgO, BeO, Al_2O_3, and ZrO_2; but the lumi-

[1]Nichols and Howes. Jour. Opt. Soc. Am., VI, p. 42, 1922; also Phys. Rev. (2), XIX, p. 300, 1922. See section I of this chapter.

nescent bands in the case of Cb_2O_5 extend through the entire spectrum and the color of the glow is a very pale blue-green. The point of lowest temperature in figure 159 represents very nearly the threshold for this type of luminescence (for Cb_2O_5), by which is meant that at lower temperatures nothing is visible and that when 640° is reached the effect appears quite suddenly.

(*c*) *Fatigue*—When a coating of the oxide not previously heated to incandescence is suddenly brought to a given temperature its initial brightness exceeds any subsequent value and it falls at first

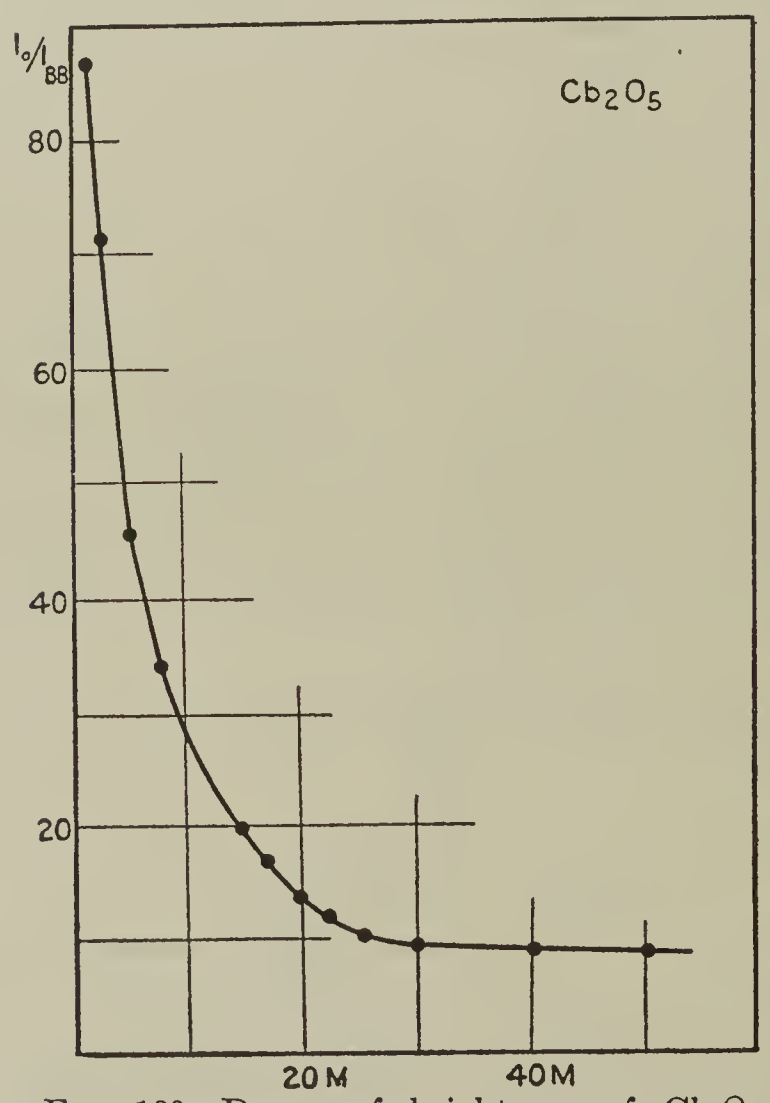


FIG. 160—Decay of brightness of Cb_2O_5 at 860° C.

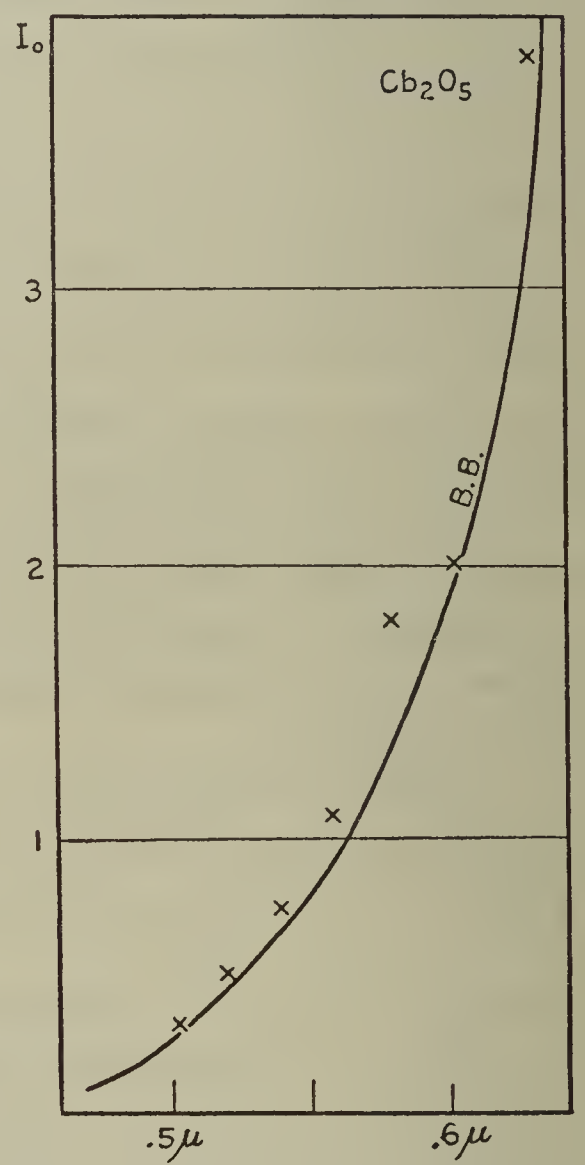


FIG. 161—Comparison of radiation (phase R) with that of black body

rapidly and then more and more slowly to a nearly constant state. This effect of fatigue, which is another of the characteristics of luminescence as distinguished from temperature radiation, is shown in the curve in figure 160, in which the abscissæ are times in minutes from the application of the flame and ordinates are intensities as expressed by the ratio I_0/I_{bb}. It will be noted by comparison with figure 159 that the brightness falls to the value for the temperature in question, *i. e.*, 860° C., after about 25 minutes.

Among the substances tested in our earlier work already described was a mixture supposed to consist chiefly of the oxides of columbium and tantalum. This was designated tentatively as niobium oxide (and wrongly as Nb_2O_4). The behavior of this substance corre-

sponded in some respects to that of Cb_2O_5. It was, for example, luminescent throughout the visible spectrum with the greatest excess of radiation in the blue-violet. It also ceased to luminesce at about 1100° C. It differed from our present oxide in showing signs of fusion just above 1100° instead of melting at 1300° and it was strongly luminescent below the threshold value of 640°. *Phase R,* if it existed, was not observed.

OBSERVATIONS ON RADIATION OF PHASE R

As has been stated in the opening paragraph of this report on Cb_2O_5, a sudden transition in the type of radiation occurs when the columbium oxide is moved from the outer oxidizing zone of the hydrogen flame into the inner reducing regions. Upon comparing the appearance of the glowing oxide with that of uranium oxide when within the reducing regions and at the same temperature, it is seen at once that the two glowing surfaces are scarcely to be distinguished either as to color or brightness.

Spectrophotometric measurements by the method used in the study of *phase O,* readings being made alternately of the brightness of the radiation from the columbium oxide (*phase R*) and from the contiguous surface of uranium oxide, confirm the impression as to the approximate identity of the two, alike in the composition of the light and as to the equality of temperature.

In figure 161 are plotted the results of such a run, taken at 954° C. The *curve* portrays the radiation from the uranium oxide at various wave-lengths; the *points marked X* show the departure of the brightness of the radiation of the columbium oxide from that of the uranium oxide. These departures, while all in the same direction, are insignificant as compared with the departures of the luminescent *phase O,* as is more strikingly shown by means of the xxx along the horizontal line in figure 158, where the radiation from the uranium oxide is taken as unity throughout the spectrum. The variation is perhaps most reasonably to be accounted for by supposing that the luminescence was almost but not entirely suppressed.

If, now, the effect of the removal of the coating across the boundary between the oxidizing and the reducing zones of the flame were merely to deprive it of the exciting action which produces luminescence, we should have a white oxide of relatively very feeble radiating power, whereas to the eye and also as determined by the optical measurements just given, it radiates *like a black body.*

The very simple explanation of this apparent anomaly is at once afforded by illuminating the glowing oxide strongly with white light when the regions from which radiation of *phase R* come *are seen to be jet black,* while the surrounding and luminescent regions in the oxid-

izing portions are a yellowish white. The boundary between black and white shifts instantly with every movement of the flame, like a shadow. Evidently the surface of the oxide within the reducing regions of the flame is converted into a black and consequently into a non-luminescent substance, probably into the black tetraoxide Cb_2O_4 known to the chemists.

ANALOGOUS CHANGES IN TiO_2 AND Ta_2O_5

After the completion of the above observation, titanium oxide, the substance first known to have two phases of radiation, and tantalum pentoxide were similarly tested. The titanium oxide darkened within the regions giving radiation of *phase R,* but the color as viewed by reflected light was a blue-gray rather than black, possibly due to the formation of Ti_2O_3. Tantalum oxide under similar conditions blackens, reducing probably to the well-known black tetraoxide Ta_2O_4.

It is probable, in view of these observations, that whenever an incandescent oxide shows two distinct types of radiation in the hydrogen flame, the effect is due to the formation of a superficial layer of a black oxide within the reducing regions of the flame whereby the luminescence of the substance is partly or entirely destroyed, while its temperature radiation proper is raised from the lower intensity characteristic of a white substance to that pertaining to a black body.

VII. NEODYMIUM OXIDE[1]

Neodymium oxide is one of the very few solids with a discontinuous spectrum. The spectrum was known, indeed, long before neodymium was separated from its fellow element præsodymium. It was briefly described by Bunsen[2] in 1864, who in the same communication mentions the discovery by Bahr[3] of the similarly banded spectrum of erbium oxide. Thus far, however, no thoroughgoing study seems to have been made of this class of spectra.

Viewed through a spectroscope of small dispersion, the spectrum of the glowing oxide, provided that the temperature does not greatly exceed 1000° C., shows six easily distinguishable bands. At higher stages of incandescence the bands merge and the spectrum can not be distinguished from that of a black body of like temperature.[4]

With the spectrophotometer a somewhat more complete resolution is obtained (fig. 162). Ten or more crests upon the brightness curve of the visible spectrum are then discernible, and these are doubtless merely envelopes of groups in a much more complicated but wholly submerged structure. Those brought out in a recent measurement

[1] E. L. Nichols. Proc. Nat. Acad. Sci., XI, p. 47, 1925.
[2] Bunsen. Liebig's Annalen, CXXXI, p. 255, 1864.
[3] Bahr. Liebig's Annalen, CXXXV, p. 376, 1865.
[4] Nichols and Howes. Physical Review (2), XIX, p. 313, 1922.

fall into two sets, such that the frequency differences between neighbors in a given set are multiples of a numerical constant which is the same for both sets. This constant is 18.5, which is the Tanaka interval[1] for neodymium, so that there would seem to be a relation between the spacing of the bands in the spectrum of glowing neodymium oxide and of those in the spectrum of cathodo-luminescent substances in which neodymium is the activating element. Having ascertained

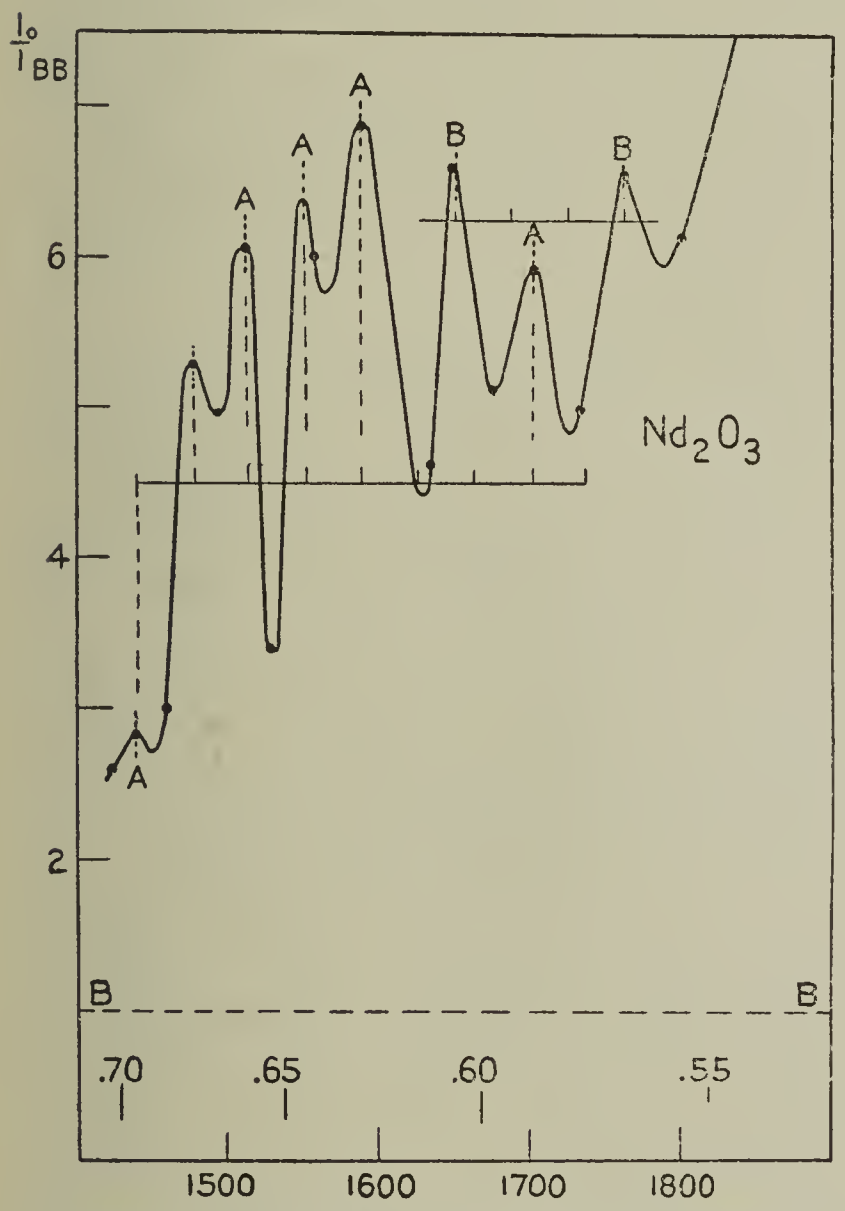


Fig. 162—Emission bands in the spectrum of glowing neodymium oxide

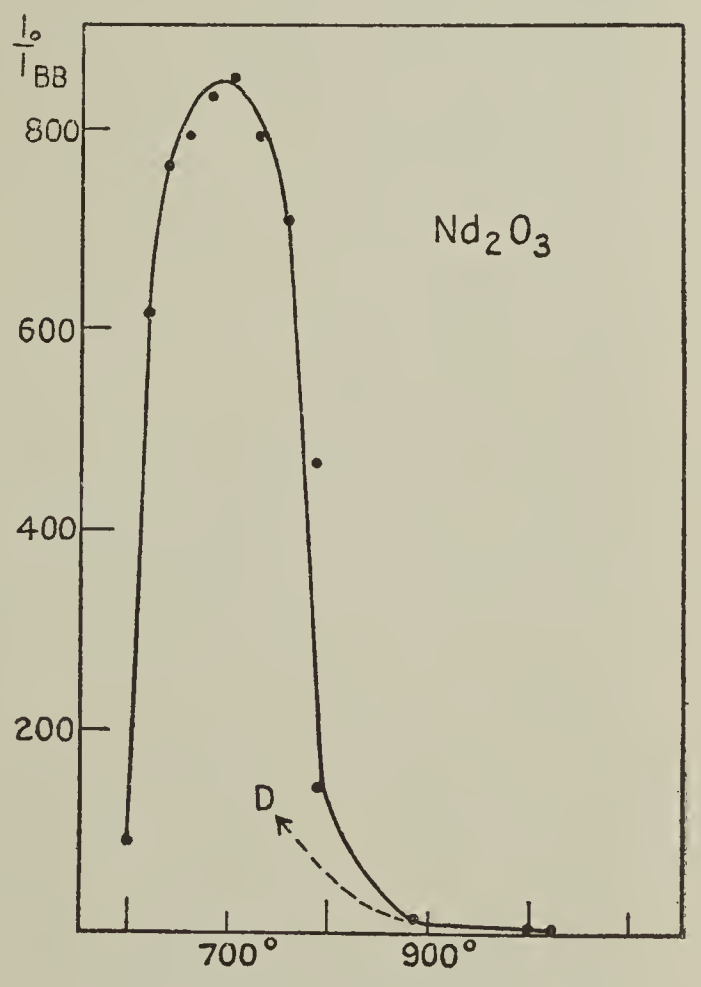


Fig. 163—Luminescence of neodymium oxide at lower stages of incandescence

by inspection that such a relation holds at least approximately, the matter is tested by constructing a scale of the interval in question and slipping it along until it matches the crests, as shown in figure 162. The dotted vertical lines crossing the crests have been drawn thus, and it will be seen that they correspond to the maxima, marked *A*, quite as closely as the data will permit these to be found. By shifting the scale slightly the second set, marked *B*, has been similarly located.

In this way the wave-lengths in table LXX have been derived

[1] Tanaka. Jour. Opt. Soc. Am., VIII, 287, 1924; see Chapter III of this treatise, table VIII.

from the spectrophotometric data indicated graphically in figure 162, where the curve of the ratio of intensity of the glowing neodymium oxide, I_0, to the brightness of the corresponding region in the spectrum of a black body at the same temperature, I_{bb}, is plotted for the longer wave-lengths of the visible spectrum (0.700μ to 0.550μ). The curve rises to ever higher values toward the violet, the ratio being 42 at the wave-length 0.4675μ.

Evidences of luminescence—To get the banded spectrum at its best and to bring out the other effects described in these notes, the oxide must be heated by direct contact with a hydrogen flame, following the procedure established in previous studies of luminescence at high temperatures. It was under such conditions that the measurements depicted in figure 162 were made.

It will be noted that the brightness of the neodymium oxide at the temperature of the experiment (about 900°) is greatly in excess of that of the black body with which it was compared. At the above temperature, therefore, there is luminescence of the oxide superimposed upon the incandescence, a condition suggested by the spectral structure described in the preceding paragraph. Above 1000° C. the banded spectrum disappears, as already noted. It is at the lowest stages of incandescence that the relative excess of brightness above that of a black body attains its maximum. This is a property common to other luminescent oxides, as has already been shown, but in most cases the effect is confined to the shorter wave-lengths. In neodymium oxide the glow extends throughout the brighter regions of the spectrum and it has been found possible to carry measurements down to temperatures below that at which the maximum of luminescence occurs. At these lowest temperatures the incandescence of the black body with which we wish to compare the brightness of the neodymium oxide is too dim for easy measurement with the optical pyrometer, and recourse is had to extrapolations based upon the following procedure: If the hydrogen flame, the axis of which is parallel to the glowing surface, be moved away stepwise, the temperature of the surface is found to be in linear relation to the distance from the axis of the flame. By a slight extension of this, straight line temperatures from 700° down to 600° are estimated.

The curve in figure 163 depicts the changes in the ratio of I_0/I_{bb} when the temperature is varied from 600° C. to 1000° C. From the lower temperature the ratio rises to its maximum value of over 800, at about 700°, then falls, rapidly at first, approaching unity shortly above 1000°. The graph applies to the group of bands in the red end of the spectrum, but similar, although not strictly identical, results are obtained for the shorter wave-lengths.

Fatigue: a further characteristic of luminescence—Neodymium

oxide when heated in the hydrogen flame shows fatigue of two kinds: (1) when heated beyond the range of temperatures indicated in figure 163—say to 1200° C.—and allowed to cool, it returns along a lower path indicated by the dotted line *D*, the position of which is determined by the duration and temperature of the previous heat treatment; (2) when maintained at any temperature at which luminescence occurs there is a falling off of brightness with the time. This second type of fatigue likewise associates incandescent Nd_2O_3 with all or nearly all other known luminescent bodies.

Bulk and bead spectra—When a bead of microcosmic salt containing neodymium oxide is brought to incandescence the emission spectrum differs markedly from that observed when the glowing oxide is in bulk instead of being in dilute suspension or possibly in solution in the molten sodium phosphate. This *bead spectrum,* as we may term it, is of interest because of its bearing upon the relation between the absorption spectrum and the emission spectrum of neodymium. Other very important bearings will be presented in Chapter XI.

An observer comparing the emission spectrum of such a bead with the absorption spectrum of the same bead when incandescent but transmitting light from behind would find the two spectra identical, as did Bunsen in the experiments cited in the opening paragraph of this section, the one spectrum being a reversal of the other. Indeed, the best way of locating emission bands in the blue, which are discerned with difficulty, is to reverse them, whereupon they stand out with great sharpness.

On the other hand, a comparison of the emission spectrum of neodymium oxide glowing in bulk with the absorption spectrum of a solution of a neodymium salt shows more apparent discrepancies than resemblances. It may, however, be shown that the "bead" spectra (emission and absorption), the absorption spectrum of solutions, and the "bulk" spectrum of the glowing oxide (as we may term it to distinguish it from the bead spectrum) all have the same structure. In a word, the *principle of essential identity* applies not only to fluorescence spectra, where we have a single activator (such as uranium or one of the rare earths) in various solutions, but extends also to the luminescence of incandescent solids, such as columbium oxide and neodymium oxide and to their absorption spectra.

The numerous determinations of the banded spectra of solutions of neodymium and the associated elements have been scrutinized by Kayser with great discrimination. If we take his list of bands belonging to neodymium[1] we find that they, too, may be arranged in sets having a common frequency interval of 18.5 (the Tanaka interval); also that two of these sets correspond to sets *A* and *B* of table LXX as to the location of their members and that the bands of the

[1] Kayser. Spectroscopie Bd. III, p. 446.

"bead" spectrum fall readily into the same system. It will be understood, of course, that these relations can be established at present only to the degree of precision with which the locations of more or less vague and often overlapping bands are known, that is to say, for the most part to 0.001μ. It is clear, however, that the various spectra of neodymium are all parts of a single structure. The relationship may be stated as follows:

(1) There are two banded emission spectra, the "bulk" spectrum and the "bead" spectrum (table LXX). Although there appear to be only two coincidences (at 1589 and 1651), each of the two spectra may be arranged in two sets, A and B, as shown in the table, and *these sets are identical,* although different places in the set are, in general, occupied by the bands of the two spectra.

TABLE LXX[1]—*Emission spectra of neodymium oxide*

	Bulk spectrum		Bead spectrum	
	$1/\mu \times 10^3$	Interval	$1/\mu \times 10^3$	Interval
Set A	1,441 (0)		1,589 (0)	
		18.5× 2		18.5× 8
	1,478 (0)		1,737 (0)	
		18.5× 2		18.5× 8
	1,515 (0)		1,885 (0)	
		18.5× 2		18.5× 7
	1,552 (0)		2,014.5 (−0.5)	
		18.5× 2		18.5× 5
	1,589 (0)		2,107 (0)	
		18.5× 6		
	1,700 (0)			
Set B	1,651 (0)		1,355 ?	
		18.5× 6		18.5× 9
	1,762 (0)		1,521.5 (+0.5)	
		18.5×12		18.5× 7
	1,984 (0)		1,651 (0)	
		18.5× 6		
	2,095 (0)			

(2) There are two absorption spectra: (*a*) that which is the reversal of the bead spectrum and may be regarded as identical with the bead spectrum in the sense that reversing spectra in general are identical; (*b*) the absorption spectrum of neodymium in aqueous solution (table LXXI). This latter shows no obvious sign of identity with either emission spectrum, there being but three coincidences (1589, 2014, and 2107), and of these, 2014 and 2107 are really coin-

[1] Numbers in parentheses denote departures from precise coincidence with the value of the corresponding member of the set to which the bands belong. As these are never more than 1 unit, while the distance between sets is of the order of 6 units, there is never any question as to the set to which a band should be ascribed.

cidences of absorption bands, since they could be located in the bead spectrum only in this reversed condition.

The *identity of structure* in the case of the absorption spectra also comes out in the fact that all the bands (29) in table LXXI can be arranged as members of the sets A and B and of a third set, C, which has the same frequency-interval and is obtained by shifting set *B* five and a half places towards the violet. Table LXXI includes all the neodymium absorption bands listed by Kayser[1] and the positions are those given by him, except as otherwise indicated. It is believed that the relation here described is common to all banded spectra of emission and absorption, but is usually concealed by the overlapping of the components.

TABLE LXXI[2]—*Absorption spectra of neodymium*

Set A		Set B		Set C	
$1/\mu\times10^3$	Interval	$1/\mu\times10^3$	Interval	$1/\mu\times10^3$	Interval
1,570.5 (+0.5)		1,355 (0)		1,451.5 (−1)	
	18.5×1		18.5× 1		18.5× 1
1,589 (0)		1,373.5 (−1)		1,470 (+1)	
	18.5×1		18.5× 9		18.5× 1
1,607.5 (0)		1,725 (−1)A		1,488.5 (0)	
	18.5×7		18.5× 1		18.5× 6
1,737 (+0.5)		1,743.5 (0)		1,599.5 (0)	
	18.5×9		18.5×12		18.5× 6
1,903.5 (0)		1,965.5 (0)		1,710.5 (0)A	
	18.5×1		18.5× 6		18.5× 1
1,922 (−0.5)		2,076.5 (0)		1,729 (−0.5)	
	18.5×5		18.5× 3		18.5× 1
2,014.5 (−0.5)N		2,132 (0)		1,747.5 (+1)	
	18.5×5		18.5× 2		18.5× 9
2,107 (0)N		2,169 (0)		1,914 (+1)	
	18.5×8				18.5×10
2,255 (−0.5)				2,099 (0)	
					18.5×11
				2,302.5 (0)	
					18.5× 5
				2,395 (0)	

[1] With the exception of three bands, the frequencies of which (1,715; 1,881.5; and 1.955.5) are evidently members of a fourth set having the same interval. The distance between sets is from 4 to 6 units.

[2] The positions listed in this table for sets A and B are calculated from sets A and B in table LXX. The numbers in parentheses denote the departures from precise coincidence on the part of the bands listed by Kayser. The values of the two bands marked A, however, are taken from Auer, and the two marked N were located in the course of our experiments on the bead spectrum. (See Chapter XI.)

CHAPTER XI

TRANSFORMATION SPECTRA

The experimental work to be described in this chapter will be considered in two parts:

(*a*) A study of the color and appearance of various molten beads when subjected to changes of temperature, particularly when the beads contained traces of various metallic elements (or their compounds in solution). These observations, which had reference to the temperatures at which certain striking transformations occurred, were made during the summer of 1923.

(*b*) A study of the spectra during these transformations when the elements introduced into the beads were of the group of the rare earths. This portion of the work was done during the summer of 1925.

I. EXPERIMENTS OF 1923

This study had its origin in a desire to determine whether the striking effects described by Lenard[1] in 1905 are related to the selective radiation and luminescence from various incandescent oxides which we were investigating in 1923.[2] Lenard finds that nearly all alkali salts, when heated in the form of a bead in the Bunsen flame, glow selectively, *e. g.*,

Cs	and	Rb	salts	yellow green
K	"	"	salts	stronger green
Na	"	"	salts	sky blue
Li	"	"	salts	pale blue

The effect begins at a fairly high incandescence (a yellow heat) and at a temperature approaching the melting-point of platinum, the colored glow goes over into white; in other words, as in the case of the oxides whose incandescence we were then studying, the selective radiation becomes non-selective at high temperatures. These colors he found to be *the same for a given metal, i. e.,* independent of the salt used, except in the case of borates and phosphates, where the phenomena are somewhat more complicated.

Lenard also studied spectrophotometrically the continuous background of the spectra of the Bunsen flame containing various salts of Cs, Rb, K, Na, and Li. The distribution of intensities was found to be *distinctive for each metal* and *independent of the acid radical.*

[1] Lenard. Ann. d. Physik, XVII, p. 199, 1905.

[2] Nichols and Wilber. Proc. Nat. Acad. Sc., VI, 693, 1920; Phys. Rev. (2), XVII, 707, 1921; Nichols and Howes, Phys. Rev. (2), XIX, 300, 1922.

Furthermore, the color of the continuous light (obtained by reassembling the continuous background of the various flame spectra) was identical with the color of the corresponding beads. These observations are of great significance from the point of view of our own work.

APPARATUS

For the Bunsen flame of Lenard we substituted a hydrogen flame issuing from an orifice about 0.25 mm. wide in a tube of nickel. The bead to be rendered incandescent was mounted from a loop of platinum wire or sometimes within a helical spiral of two or more turns. The helical mounting was used with salts which did not cling securely to a hot wire or when a greater depth of the molten material was desired. In the study of absorption spectra this device was especially advantageous, because the faces of the bead perpendicular to the axis of the helix could be made flat and nearly parallel, giving an approximately cylindrical instead of a lenticular body.

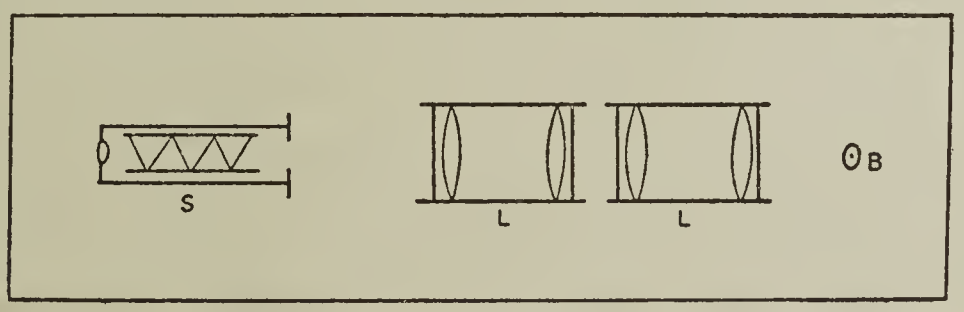


FIG. 164—Direct-vision spectroscope and lens system

A V-shaped, Pt-PtRh thermo-element with the junction at the apex was so mounted that the tip was submerged within the mass of the bead. In some cases the bead could be hung to the thermo-junction itself without other support, thus dispensing with the platinum loop or helix. The wires of this thermo-element were about 0.25 mm. in diameter. If much thinner they are apt to melt off in the flame; if much thicker the bead does not reach the highest temperatures desired.

While such thermo-elements are ill-adapted to the measurement of the temperatures of gases within a flame, they will give quite accurately the temperature of a bead in which the junction is submerged, especially when the bead is molten. We found, for example, that when beads of LiF, RbF, NaF, NaCl, Na_2SO_4, and $Na_2P_2O_7$ were mounted in the flame with the junction submerged as above described, they fused when the temperature as indicated by the thermo-element reached the known melting-point of the salt. The agreement, indeed, was surprisingly good, in general within one or two degrees centigrade.

Observations of the color of the bead and of the transformations which it underwent with change of temperature were made in a darkened room with the unaided eye or sometimes by the use of an

enlarged image. Temperatures were taken with a potentiometer in the circuit of the thermo-element. To study the spectrum, an enlarged image of the bead *B* was projected upon the slit of a hand spectroscope, *S* (fig. 164) by means of a system of large lenses, *L, L*. With this device, instead of a spectrum of the light from the bead as a whole, a considerable amount of detail was obtainable and one could observe, for example, the spectra of separate particles floating around within the bead at times when the latter was beginning to cloud up or to clarify.

The adjustment of the apparatus was greatly facilitated by mounting the flame with a horizontal micrometer movement so that its position relative to the bead could be smoothly varied without disturbing the place of the bead in front of the lens system.

REPETITION OF LENARD'S EXPERIMENT

To see in how far Lenard's results could be obtained with our apparatus, a bead of NaF was mounted in a platinum loop and the H flame was moved up laterally with the micrometer-screw. As the temperature of the bead rose it became molten and clear, showed the blue color described by Lenard, then clouded with a red turbulent precipitate, and finally began to glow with a white light which soon approximated the color and brightness of the platinum wire. On lowering the temperature there was a complete reversal of the phenomena.

Temperatures of the bead as indicated by the thermo-element were as follows:

Rising temperature		Falling temperature	
	° *C.*		° *C.*
Blue appears at.....	995	Red cloud vanishes at....	1,210
Observation repeated.....	995	Observation repeated....	1,207
Red cloud appears at.....	1,205	Blue vanishes at.....	990
Observation repeated.....	1,210		

At 1287° the "white glow" of the bead approximated that of the platinum wire in color and brightness.

A naked junction in the outer layers of the hydrogen flame fluctuated between 1400° and 1500° with slight movements of the flame. When a bead about 2 mm. in diameter was suspended from the junction, submerging it, the temperature fell to 1170°, at which point it remained quite constant. The combined heat losses by radiation and evaporation suffice to maintain the bead at a constant temperature 200 or 300 degrees below the average temperature of the surrounding gases.

The spectrum of the bead was continuous, save for the Na lines, but the distribution was not that of a black body. A detailed spectrophotometric analysis would doubtless reveal details of structure, but to the eye it appeared to consist of a single broad band extending respectively:

In the red phase, 0.700 to 0.485, brilliant in red; green, bright; blue-violet nearly absent.
In the blue phase . . . to 0.425; red, *nearly absent;* green, dim; blue-violet, medium. Crest at about 0.450.

Similar transformations, *i. e.*, from blue to red, were observed in a bead of NaCl (from Louisiana rock salt), but no quantitative determinations were made. Similar experiments with beads made from various salts of Li, K, and Rb served to confirm Lenard's statements as to the colors characteristic of those elements. It is of interest to note that the relation between color and the atomic weight is similar to that found by Tanaka[1] in the case of the fluorescence colors of certain solid substances. In Chapter VI[2] a similar relation has been shown to exist in the case of the fluorescence of solids in which a trace of uranyl served as an activator. Attention is called to this relation here because it affords a suggestion, of no obvious significance in itself, as to a possible explanation of the nature of certain effects in the incandescent beads to be considered in section II of this chapter.

Measurements of the temperatures at which these color effects occur in the various beads and of the phenomena preceding and following them bring out the fact quite clearly that the colors are definitely connected with *transformations* which take place within the molten material. In most instances, however, the color effect is only one of a more or less complicated series of changes which go on within the bead. The record in the case of LiF, for example, which was quite consistent on repetition both as to the temperatures at which changes occur and the accompanying phenomena, was as follows:

When cold, the bead is clouded and almost white.
At 642° it turns black (as viewed by reflected light).
At 651° the above change is completed.
At 662° the bead clears up and becomes transparent.
At 801° the bead fuses (the melting-point as given in the tables of Landolt and Börnstein is 801° ± 15°).
At 900° turbulence sets in, opaque masses form within the bead, which becomes clouded and remains so until —
At 1085° it again clears with a light-blue color which suggests the opalescence of a moonstone.
At 1310° the blue disappears.

The blackening of the bead noted above in the case of LiF as occurring between the narrow limits 642° to 662° was observed also in beads of Rb_2SO_4 at 585° and of $BaCl_2$ for the much wider range

[1] T. Tanaka. Jour. Opt. Soc. Am., VIII, 287-318, 1924. See also Chapter III of this treatise.
[2] See also Nichols and Slattery. Jour. Opt. Soc. Am., XII, p. 449, 1926.

between 350° and 680°. The effect is of course merely an indication that the bead passes from complete transparency to a high degree of absorption of visible radiation and vice versa at the upper and lower limits. At higher stages of incandescence this condition would manifest itself by a non-selective glow of the sort characteristic of black-body radiation proper to the temperature in question. That under illumination sufficient to overpower the emitted light such substances will appear black is obvious.[1] Color as described in the present chapter, however, except in the case of beads at temperatures below the red heat, is the color of incandescence, *i. e.*, the color of the bead as it appears in a dark room by virtue of its own emitted light.

With the alkaline salts the material for the study of the radiation from molten beads is virtually exhausted. $BaCl_2$, which has just been mentioned, forms a clear molten bead which is bright blue when first heated to about 1200°, and there are probably other examples, but for the most part one must go to higher temperatures than are obtainable with a platinum wire in a hydrogen flame. Having in mind, however, that in the domain of luminescence many solids which are non-luminescent when taken in bulk at ordinary temperatures become activators of luminescence when in extremely dilute solid solution, and that on the other hand nearly all refractory oxides which are white or nearly so radiate selectively at the lower ranges of incandescence (500° to 1200°) in a manner which we are compelled to describe as a type of luminescence, it seemed worth while to examine the radiation of beads in which a trace of various oxides or other salts had been dissolved.

The solvent selected for this purpose was $Na_4P_2O_7$ produced by heating Na_2HPO_4. Into beads of this composition salts of numerous elements were introduced and the effects of heating were noted.

A bead of sodium phosphate, without admixture, goes through its transformations and color-changes like those described in the earlier paragraphs of this paper, and it was for modifications in these effects that we proposed to look. The transformations and color effects with this sodium phosphate bead are fortunately quite simple, viz (*bead cooling*):

1320°, clear and colorless
1278°, begins to cloud up
1220°, uniformly cloudy but not opaque
1086°, begins to clear
957°, (melting-point), clouds up with a fine lemon-yellow color.

After solidification the bead remains clouded, glasslike, colorless. Here the only transformation accompanied by color is *that at the melting-point,* and, as long since noted by Lenard, the color is not the blue characteristic of the other sodium salts.

[1] Nichols and Howes, l. c.

The elements, from whose presence in the bead results of interest might be anticipated, were taken, for convenience, in the following four groups (see table LXXII):

(A) Well-known activators of luminescence (Bi, Cr, Cu, Mn, U).

(B) Elements whose white, refractory oxides are luminescent at temperatures of incandescence (Al, Be, Ca, Mg, Si, Ti, Zr).

(C) Elements notable as selective radiators (Ce, Er, La, Nd, Th).

(D) The rare-earth elements (Dys, Gd, Ho, Sa).

In addition to the above, a cursory test was made of salts of the following elements: Ag, As, Ba, Cd, Co, Fe, Ga, Ge, Hg, Mo, Ni, Pb, Sn, Sr, Ta, Tl, Va, W.

TABLE LXXII—*Transformation temperatures of beads* ($Na_4P_2O_7$)

Group	Element in solution	Temperature of transformers	Transformation	Color change
		° *C.*		
(A) Activators of luminescence	Bi.....	957	Bead melts; clear.....	Dark red
		1,046	Bead cloudy.....	Bright yellow
			Bead clears.....	
		1,220	Bead cloudy (blue streamers)[a]	Blue
			Bead clears.....	
		1,312	Bead cloudy.....	Bright yellow-red
	Cr.....	957	Bead melts (red flash on sudden cooling).....	Faint blue
		1,050	Bead clear.....	
		1,260	Bead clouding up.....	Ruddy
		1,400	Bead cloudy; very bright.....	White
	Cu (form of CuO)	957	Bead melts (red flash on cooling)..	Red
		990	Bead clouding.....	Orange
		1,122	Bead clouded.....	Bright yellow
		1,212	Bead clearing (blue steamers).....	Bright blue
		1,235	Bead very clear, colorless and dark	
	Mn.....	957	Bead melts.....	
		1,060	Bead cloudy.....	Orange yellow
		1,200	Bead cloudy.....	Ruddy
		1,330	Bead clears up.....	Blue
	U (1 p ct of $UO_2P_2O_7$)	957	Bead melts; cloudy.....	Yellow
		1,112	Bead still cloudy.....	Green
		1,208	.....	Still green
		1,308	Bead clearing.....	Red
		1,370	Bead clear.....	Bright red
	Zn (form of ZnO)	957	Bead melts; cloudy.....	Red
		1,130	Bead clearing (blue streamers)....	Blue
		1,170	Bead clear.....	Ruddy
		1,300	Bead clear.....	Ruddy

[a] The effect designated by the term "blue streamers" consists of the formation of a moving cloud within the clear body of the bead. The color of the cloud is that of the blue of a finely divided medium, and marks the transition from clear to cloudy or vice versa.

TABLE LXXII—*Transformation temperatures of beads* ($Na_4P_2O_7$)—Continued

Group	Element in solution	Temperature of transformers	Transformation	Color change
		° *C.*		
(B) Elements whose oxides show luminescence at high temperatures	Al (form of Al_2O_3 very dilute)	1,009	Bead melts; (clouds on freezing; clears on melting)	
		1,078	Bead clouding	Ruddy
		1,296	Bead clouded	Ruddy
		1,357	Bead clearing (blue streamers)	Blue
		1,397	Bead clear	
	Be (1 p ct BeO)	20	Bead clear	Pale blue-green
		720	Bead clear, turning purple on heating	A deeper blue
		955	Bead melts (on freezing, a red precipitate with turbulence within the bead)	Purple
		1,045	.....	Ruddy color is vanishing
		1,220	Bead clear	Blue
		1,287	Bead brighter	
		1,312	Bead slightly cloudy	Ruddy
	Ca (trace of $CaSO_4$)	957	Bead, which is clouded when solid, melts and clears	Faint pink
		1,275	No change until this, then turbulence	Ruddy
		1,300	Bead clearer	Deeper red
	Mg (trace of MgO)	1,040	Bead melts; clouded	Ruddy
		1,125	Bead clouded, bright	Yellow
		1,300	Bead clearing (blue streamers)	Blue
		1,397	Bead clear	
	Si (trace of SiO_2)	1,000	Bead melts; partly clouded	
		1,220	Bead clouds up completely	Yellow-orange
		1,353	Bead clearing (blue streamers)	Blue
		1,400	Bead clear	Ruddy
	Ti (trace of TiO_2)	957	Bead melts	
		1,062	Bead clearing	Very blue
		1,220	Bead clear	Yellow
		1,329	Bead clouding	Ruddy
	Zr (trace of ZrO)	1,054	Bead solid; clouded, bright	Yellow-white
		1,170	Bead melts and clears	
		1,191	White streamers	
		1,300	Bead clear	Ruddy
(C) Selective radiators	Ce (trace of CeO)	955	Bead melts, goes over from deep red to yellow on fusion	Red / Yellow
		973	Bead changing to green	Green
		1,249	Bead clears (blue streamers)	Blue
	Er	1,000	Bead melts; clouded	Yellow-white
		1,220	Bead clearing (blue streamers)	Blue
		1,355	Bead very clear	
			NOTE: Emission bands of erbium are finely visible at the lower temperatures	

TABLE LXXII—*Transformation temperatures of beads* ($Na_4P_2O_7$)—Continued

Group	Element in solution	Temperature of transformers	Transformation	Color change
		° *C.*		
(C) Selective radiators—Con.	La ($La(NO_3)_3$)	Cold	Bead is opaque	White
		1,045	Bead melts	
		1,086	Bead clearing	Bright yellow
		1,286	Bead clouded (blue streamers)	Blue
		1,312	Bead very clear	
	Nd (oxalate)	957	Bead melts; while solid is	Lavender
			Bead clouded throughout; no sudden transformations	Pale purple
		1,260	Bead very bright	Ruddy
			NOTE: Bead shows the well-known emission bands of neodymium, especially well at lower temperatures	
	Th ($Th(NO_3)_4$)	1,094	Bead melts	
		1,135	Bead clears	Blue
		1,220		Blue is gone
		1,329	Bead very clear	
(D) Rare-earth elements	Dys	Cold	Bead white like enamel	White
		957	Bead melts	
		995	Bead clouding up	Ruddy
		1,125	Bead clouded, bright	Yellow
		1,220	Bead clearing	
		1,240	Bead clear, dark	
		1,280	Bead clear, dark	
	Gd	957	Bead melts	
		1,040	Bead clear, dark	
		1,125	Bead clouding up (blue streamers)	Blue
		1,260	Bead clearing (blue streamers vanish)	Blue vanishing
		1,300	Bead clear, bright	Yellow
	Ho	957	Bead melts	
		995	Bead clouding up	Ruddy
		1,040	Bead clouded	Red-yellow
		1,175	Bead clouded	Yellow
		1,220	Bead clearing (white streamers)	
		1,260	Bead turbulent	Ruddy
		1,355	Bead slightly cloudy, bright	Yellow
	Sm	957	Bead melts	
		1,015	Bead clear	Ruddy
		1,080	Bead clouding up	Yellow
		1,175	Bead clouded, bright	Yellow
		1,340	Bead clearing	Red-yellow
(E) Miscellaneous beads	Ag (trace of $AgNO_3$)	957	Bead melts	
		1,045	Bead clear, dark	
		1,125	Bead slightly cloudy (blue streamers)	Blue
		1,280	Bead very clear and dark	

TABLE LXXII—*Transformation temperatures of beads* ($Na_4P_2O_7$)—Continued

Group	Element in solution	Temperature of transformers	Transformation	Color change
		° *C.*		
(E) Miscellaneous beads—Con.	As (trace of As_2O_3)	990	Bead melts	
		1,086	Bead clouding	
		1,220	Bead cloudy	Yellow
		1,312	Bead clearing (blue streamers)	Blue
		1,396	Bead slightly cloudy, bright	Yellow
	Ba (trace of BaO)	999	Bead melts	
		1,239	Bead clear, very red	Red
		1,300	Bead cloudy, bright	Yellow
		1,320	Bead cloudy	Ruddy
	Cd (traces of phosphate)	998	Bead melts	
		1,215	Bead clouding	No striking color effects
		1,240	Bead clears again	
	Cr, Cr_2O_3 (trace)	957	Bead melts (red flash on cooling)	Red
		1,040	Bead clear; very slight color	Blue
		1,260	Bead clouding	Ruddy
		1,400	Bead clouded; very bright	White
	Fe (trace of FeO)	Cold	Bead gray-yellow, becoming black on heating	
		950	Bead melts	Red
		1,040	Bead opaque	Orange-red
		1,145	Bead clearing	Orange-yellow
		1,300	Bead clear (blue streamers, dark-red bead)	Orange-yellow
	Ga (trace of the oxide)	Below 1,365	Bead clear	
		1,365	Bead clouds	Blue-white
		1,375	Bead clears again	
	Hg (trace of $HgSO_4$)	957	Bead melts	
		1,015	Bead cloudy (red streamers)	Red
		1,040	Bead clear	Yellow
		1,125	Bead slightly cloudy, bright	Yellow
		1,220	Bead clear, dark, ruddy	Ruddy
	Pb (trace of PbO)	Cold	Bead bluish gray	Gray
		950	Bead melts and clears; red before fusing	Red
		1,125	Bead clear, turning blue	Blue
		1,400	Bead still clear	Purple
	Sn (trace of SnO_2)	Cold	Bead is blue	Blue
		957	Bead melts	Ruddy
		1,100	Bead clear, bright	Yellow
		1,173	Bead clouding (blue streamers)	Blue
		1,312	Bead clouded	Red
	Sr (trace of $SrCO_3$)	1,027	Bead melts	
		1,045	Bead slightly clouded	Ruddy
		1,220	Bead clearing (blue streamers)	Blue
		1,380	Bead very clear, very dark	

TABLE LXXII—*Transformation temperatures of beads* ($Na_4P_2O_7$)—Continued

Group	Element in solution	Temperature of transformers	Transformation	Color change
		° *C.*		
(E) Miscellaneous beads—Con.	Ta.....	Cold	Bead opaque.....	White
		957	Bead melts, clouded.....	Yellow
		1,086	Bead clearing.....	Yellow-green
		1,145	Bead clear.....	Blue
		1,278	Bead clear, very blue.....	Blue
		1,320	Bead clear, blue with ruddy tinge..	Blue-ruddy
		1,329	Bead clear, very blue	
	Tl (trace of $TlCl_3$)	957	Bead melts clear	
		980	Bead clouding up	
		1,125	Bead clouded.....	Yellow
		1,220	Bead clearing.....	Ruddy
	Va (trace of $VaCl_3$)	957	Bead melts	
		1,046	Bead clear, dark	
		1,102	Bead very clear.....	Green
		1,126	Bead clouding up.....	Yellow
		1,220	Bead opaque.....	Red-yellow
	W (trace of oxide)	957	Bead melts	
		1,200	Bead clouding up	
		1,220	Bead clouded (turns red).....	Red
		1,268	Bead very clear	

Of all the beads tested in the course of these experiments the only ones failing to show indications of transformation were those containing germanium, molybdenum, nickel, and cobalt. On the other hand, the most interesting and important effects were not brought out until the adoption of the method of flame extinction in 1925.

II. EXPERIMENTS OF 1925

In the summer of 1925 two of the writers, Nichols and Howes, returned to the study of the color effects in beads from a somewhat different point of view. It was clear from the observations of 1923 that the appearance of color was directly connected with reactions taking place at definite temperatures. In the meantime, it had been shown that certain of the rare earths in solid solution, when bombarded by cathode rays, yielded fluorescence spectra of an extraordinary character. The luminescence bands of these substances are so narrow and line-like that the spectra resemble flame spectra rather than the usual spectra of solids. To produce analogous spectra at temperatures of incandescence, if possible, and to compare these with the luminescence spectra in some definite way, was the purpose of these later experiments.

The clear-cut and strikingly beautiful way in which, in 1923, the emission bands of neodymium had been observed to come out, when beads containing that element were removed from the flame and allowed to cool, suggested a promising procedure for the new attempt.

Apparatus

The apparatus depicted in figure 164 was mounted in a room well darkened and the bead to be examined was adjusted in the hydrogen flame with its image carefully focussed upon the slit of the spectroscope. An observer whose eye had been rendered properly sensitive by previous protection from light seated himself at the eye-piece, the bead was brought to its maximum temperature, about 1400°, by increasing the supply of hydrogen, and, with the observer's attention fixed upon the spectrum, the flame was suddenly extinguished (or reduced to a mere pilot flame).

As the bead passed through the temperature of transformation, in general there was a more or less sudden *increase in brightness.* Sometimes this amounted to a veritable flash-up, as in the case of lanthanum; sometimes it was scarcely perceptible when looking directly at the bead itself. In the field of the spectroscope the effect sometimes amounted simply to a general momentary brightening of the whole visible spectrum, or a relative enhancement of some region, as the blue, green, or red.

Sometimes, when the bead contained a rare earth in solution, narrow bands appeared in the rapidly darkening field and then faded away. These were very like those that characterize the luminescence spectrum of the element. There was something weird about the apparition of these bands. Here we had the *transformation spectrum* for which we were looking.

Once discovered, the new effect became less and less obscure, and with practice the bands could also be picked up on rising temperatures. With practice, too, it became possible to locate the bands by means of the wave-length scale in the eye-piece of the spectroscope and thus to make a long-desired comparison between the radiation of these substances at temperatures of incandescence with the luminescence due to cathode bombardment at ordinary temperatures.

LUMINESCENCE SPECTRA AND TRANSFORMATION SPECTRA

Thulium—When a trace of this element was put into solid solution in calcium fluoride and excited to luminescence by cathode bombardment, a spectrum of narrow line-like bands was obtained. (See fluorescence bands listed in table LXXIII.) When the transformation spectrum of a bead containing thulium was observed by the process of quenching already described, bands recorded in the same

table were noted. The two spectra have but one band in common, that at 1928, but in the sense in which that term is used[1] in the present study of luminescence spectra, they are "essentially identical." The principle here referred to may be restated as follows:

THE PRINCIPLE OF ESSENTIAL IDENTITY

(1) Two spectra are *essentially identical* when all their components are members of the same set or sets.

(2) A *set* (as used here) is an aggregate of equidistant components where distance is measured by frequency units.

(3) A *full set* is a set in which all members, between the two outer limits of the spectrum, are present.

(4) An *incomplete set* is one with missing members, but in which distances between existing members are always exact multiples of the frequency interval. Sets in the spectra of solid solutions are in general incomplete.

TABLE LXXIII—*Transformation and fluorescence bands of thulium*

Set A		Set B	
$1/\mu\times10^3$	Δ	$1/\mu\times10^3$	Δ
1,515 (fluor)			
	111= 7×16−1		
1,626 (fluor)			
	98= 6×16+2	1,667 (trans)	
1,724 (fluor)			
	49= 3×16+1		
1,773 (fluor)			
	64= 4×16		256=16×16
1,837 (fluor)			
	32= 2×16		
1,869 (fluor)			
		1,923 (both)	
			15= 1×16−1
	272=17×16	1,938 (trans)	
			190=12×16−2
		2,128 (trans)	
2,141 (fluor)			
	96= 6×16		
2,237 (trans)			
	144= 9×16		
2,381 (trans)			

(5) The spectra to which this definition applies are spectra made up of bands either separate or overlapping. The structure in question has been found to occur even where the overlapping is so complete that components are entirely submerged and the spectrum appears to be continuous.

[1] Nichols and Howes. J. Opt. Soc. Am., XIII, p. 586, 1926. See also pp. 3 and 4 of this volume.

Europium—The emission of this element *in borax* is somewhat more complicated than in the case of thulium. Upon heating the bead the following effects are observed: At 820° C. the bead glows *orange, clouded;* at 940° the bead clears; at 1085° the bead is clear, *green;* at 1145° the bead is a brilliant green. Upon cooling there is a distinct flash-up of green at 1050°. In the spectrum both red and green bands come out between that temperature and 920°, with crests at 0.630μ (1,587), 0.562μ (1,779), and 0.530μ (1,887). At a still lower temperature (760°) an *orange* band appears. This orange band is in two parts, a component (*a*) narrow and sharp, at 0.601μ (1,664) and a somewhat broader portion (*b*) with shaded edges and a crest at 0.608μ (1,645). Component (*a*) is only seen when the flame is suddenly quenched and disappears almost at once. Component (*b*) persists to much lower incandescence and can sometimes be seen on rising temperatures also.

TABLE LXXIV—*Transformation and fluorescence bands of europium*

Set A		Set B	
$1/\mu\times10^3$	Δ	$1/\mu\times10^3$	Δ
		1,538 (fluor)	
			54= 3×18
		1,592 (fluor)	
1,600 (fluor)			18= 1×18
	18= 1×18	1,610 (fluor)	
1,618 (fluor)			35= 2×18−1
		1,645 (trans)	
	161= 9×18−1		19= 1×18+1
		1,664 (*both*)	
			19= 1×18+1
		1,683 (fluor)	
1,779 (*both*)			
	36= 2×18		
1,815 (fluor)			
	72= 4×18		
1,887 (*both*)			
	55= 3×18+1		
1,942 (fluor)			
	107= 6×18−1		
2,049 (fluor)			

Comparing these bands with the luminescence spectrum of europium, we find: (*a*) That the green bands of the flash-up at 1050° are members of set A of the luminescence spectrum and both coincide with observed members of that set, (*b*) that crests of the orange bands at 760° belong to set B of that spectrum, the component 1,664 being coincident with an observed luminescence band of that set. The frequency distance to the other component, 1664—1645=19, is within the errors of observation of these necessarily rough settings. (See table LXXIV.)

As to the band in the red seen at the higher transformation-point and recorded as at 0.630μ, the chances favor the existence of a double crest with a frequency difference of 18, which, being insufficiently resolved, was taken to be a single crest of intermediate location. Whether this doublet belongs to set A or set B can not be ascertained from the existing reading. An error of setting of five frequency units is unlikely. The existence of a band belonging to an entirely different system, perhaps to a different activator, is by no means excluded.

Terbium in borax develops several bands on cooling. The bead has a transformation at 900° characterized by a green flash-up. Of the seven transformation bands which were located, five are identical with actual fluorescence bands (see table LXXV); another occupies a vacant place in set A. The seventh, 0.530μ (1,887) is found in the fluorescence spectra of terbium, samarium, and europium, but is probably due to the presence of a trace of europium.

TABLE LXXV—*Transformation and fluorescence bands of terbium*

Set A		Set A′	
$1/\mu\times10^3$	Δ	$1/\mu\times10^3$	Δ
		1,645 (fluor)	
			64= 4×16
		1,709 (fluor)	
			15= 1×16−1
		1,724 (fluor)	
1,739 (both)			
	31= 2×16−1		
1,770 (fluor)			
	16= 1×16		
1,786 (fluor)			
	16= 1×16		
1,802 (fluor)			304=19×16
	16= 1×16		
1,818 (both)			
	143= 9×16−1		
1,961 (both)			
	47= 3×16−1		
2,008 (trans)			
	49= 3×16+1	2,028 (fluor)	
1,057 (fluor)			
	31= 2×16−1		
2,088 (fluor)			209=13×16+1
	17= 1×16+1		
2,105 (trans)			
		2,237 (both)	

Samarium in borax gave six bands during the transformation stages which could be positively located. There were indications of others which would probably be amenable to setting under more favorable conditions. Of those which we succeeded in placing, three

coincide with known fluorescence bands, while all fall into the sets previously established for this element. (See table LXXVI.)

The observer at the eye-piece of the spectroscope announced the appearance of the *green doublet,* 0.567μ–0.572μ, at a cooling temperature of 1050°. At 1000° these bands disappeared and were replaced by the red band with crest at 0.648μ, which remained visible until the bead had cooled to 860°. By reference to table LXXII (D), it

TABLE LXXVI—*Transformation and fluorescence bands of samarium*

Set A		Set B	
$1/\mu\times10^3$	Δ	$1/\mu\times10^3$	Δ
1,563 (fluor)		1,475 (fluor)	
		1,539 (fluor)	64= 4×16
		1,554 (fluor)	15= 1×16−1
		1,617 (fluor)	63= 4×16−1
		1,664 (trans)	47= 3×16−1
	161=10×16+1	1,681 (fluor)	17= 1×16+1
1,724 (fluor)		1,712 (fluor)	31= 2×16−1
	15= 1×16−1		
1,739 (fluor)			65= 4×16+1
	31= 2×16−1		
1,770 (fluor)			
	32= 2×16	1,777(fluor)	64= 4×16
1,802 (fluor)		1,841 (fluor)	
		2,128 (*both*)	287=18×16−1

Set C		Set C^1	
		1,541 (*both*)	
1,607 (fluor)			112= 7×16
	32= 2×16	1,653 (fluor)	
1,639 (fluor)			
	16= 1×16		48= 3×16
1,655 (fluor)			
	17= 1×16+1	1,701 (fluor)	
1,672 fluor)			47= 3×16−1
		1,748 (trans)	
	159=10×16−1		16= 1×16
		1,764 (*both*)	
			64= 4×16
1,831 (fluor)		1,828 (fluor)	
	49= 3×16+1		
1,880 (trans)			

will be seen that within the former range a transformation of the bead from *clouded* to *clear* was recorded (color, yellow). Within the range 1000°–860° the bead congeals and the color is described as *ruddy*.

SUMMARY

(1) The observations of Lenard upon the colors of molten beads were confirmed and the temperatures at which the effects occur were determined.

(2) Observations upon 37 elements whose salts can not readily be obtained in the form of molten beads were made by introducing a small quantity of a compound of the element to be studied into beads of sodium phosphate, or sometimes of borax.

(3) Such beads heated in a hydrogen flame were found to undergo transformations characterized by a sudden clouding or, vice versa, a sudden clearing of the bead, which changes occur at definite temperatures.

(4) These transformations are further marked by changes of brightness and frequently by a characteristic color which is present only during the stage of transformation.

(5) The effects are reversible, *i. e.*, may be observed either during heating or cooling of the bead.

(6) The *spectra* of the glowing beads are, in general, continuous or at least broad-banded. Where traces of erbium or of neodymium are used, however, the well-known emission bands appear.

(7) *During transformation* there is a brightening of the whole visible spectrum or of some special region (red, green, or blue.)

(8) When the bead contains a rare earth element the *transformation spectrum* (best observed during cooling) *consists of narrow bands.*

(9) These bands correspond to those of the cathodo-fluorescence of the element as to location, so that *transformation spectra* and *fluorescence spectra* are *"essentially identical."*

CHAPTER XII

LINKS CONNECTING FLUORESCENCE AND THE LUMINESCENCE OF INCANDESCENT BODIES (CANDO-LUMINESCENCE)

I. EARLY EXPERIMENTS

Thirty-five years ago, in June 1891, one of the present writers, in collaboration with B. W. Snow,[1] called attention to the remarkable departures of zinc oxide from the laws of ordinary temperature radiation. Since these departures were in the nature of an *excess,* the then new term *luminescence,* proposed by Eilhardt Wiedemann for any type of radiation not the direct result of temperature, was used to designate them.

It was established at that time that the effect was selective as to wave-length, was confined to a rather narrow range of temperatures, and was subject to fatigue; statements which may be illustrated by the figures following, made from measurements in the course of that investigation and later. Figure 165 gives the distribution of brightness in the visible spectrum of glowing zinc oxide at three temperatures in terms of that of a black body taken as unity. The dotted horizontal line *BB* represents normal black-body radiation and ordinates are the ratio I_0/I_{bb} where I_0 is the intensity of the oxide. A white oxide is normally a poor radiator, which condition is expressed by the curve for the radiation at 692° C., but at 848° and 1013° we see the development of a band having its crest in the violet, with a suspicion of a shoulder in the yellow which suggests a second overlapping band. The intensities of the crest run to more than twice the corresponding black-body brightness, whence the designation of the effect as luminescence. In the foregoing chapters of this treatise are many further examples, and figure 165 is given only because it represents what are thought to be the earliest measurements of this effect. The similar outburst which constitutes the extraordinary actinic intensity of the magnesium flame and which has been shown to be due to the luminescence of the nascent particles of MgO within the flame was later studied by F. J. Rogers.[2]

Fatigue—The falling off in brightness which characterizes ordinary luminescence is also a feature of the luminescence of incan-

[1] Nichols and Snow. Phil. Mag. (5), XXXIII, p. 21, 1892. This is ancient history. We recall it here because in this final chapter we propose to bring together whatever has a bearing upon the relation of the luminescence of incandescent bodies (cando-luminescence) to luminescence at ordinary temperatures. To this end we shall venture to repeat many familiar matters some of which have already been discussed in the earlier chapters of this monograph.

[2] F. J. Rogers. Am. Jour. Sc., XLIII, p. 301, 1892.

descent solids. The curve in figure 166, which is from the measurements of 1891, refers to the violet end of the spectrum, but similar curves may be plotted from the existing data for any chosen wavelength. The phenomenon was familiar to every user of the lime-light in the rapid fading away of that source of illumination, which required frequent turning of the cylinders of lime so as to expose new surfaces to the flame. Measurements[1] made of the decay of the lime-light for different parts of the spectrum led to a similar result to that for ZnO. In this case it was found that complete return of the material to its original state occurred upon resting, a property which is also characteristic of ordinary fluorescence.

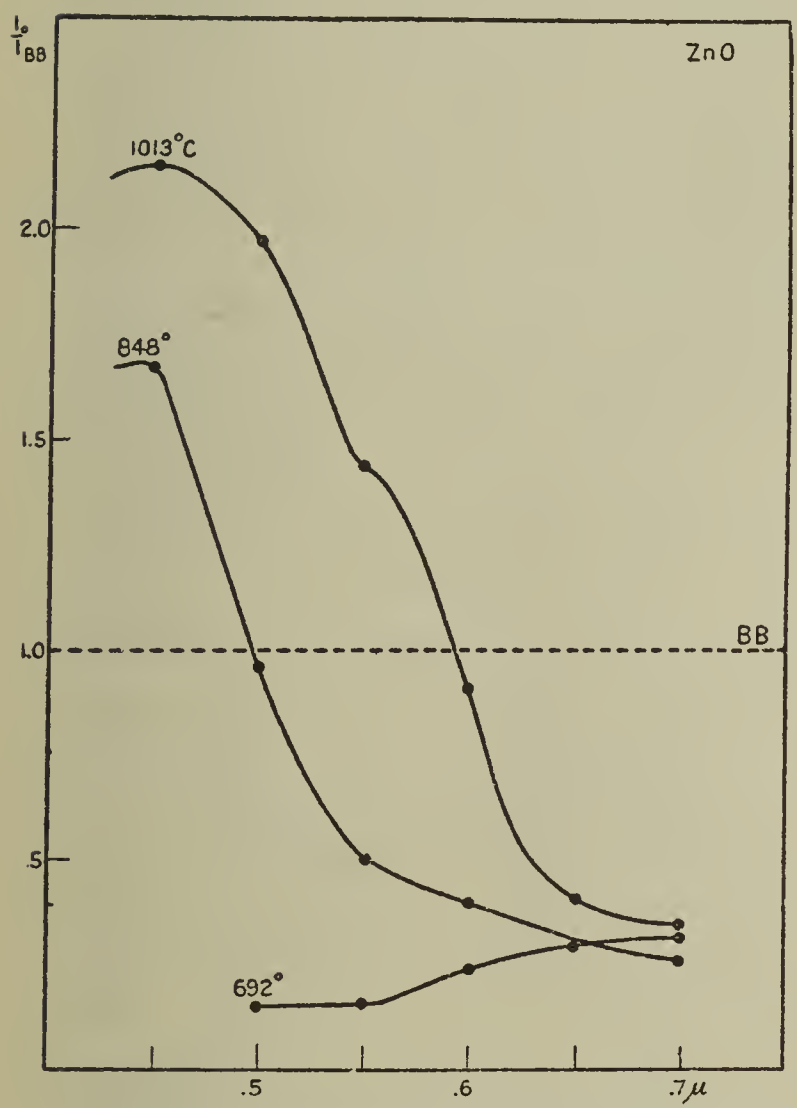


FIG. 165—Development of selective radiation (luminescence). From data of 1891

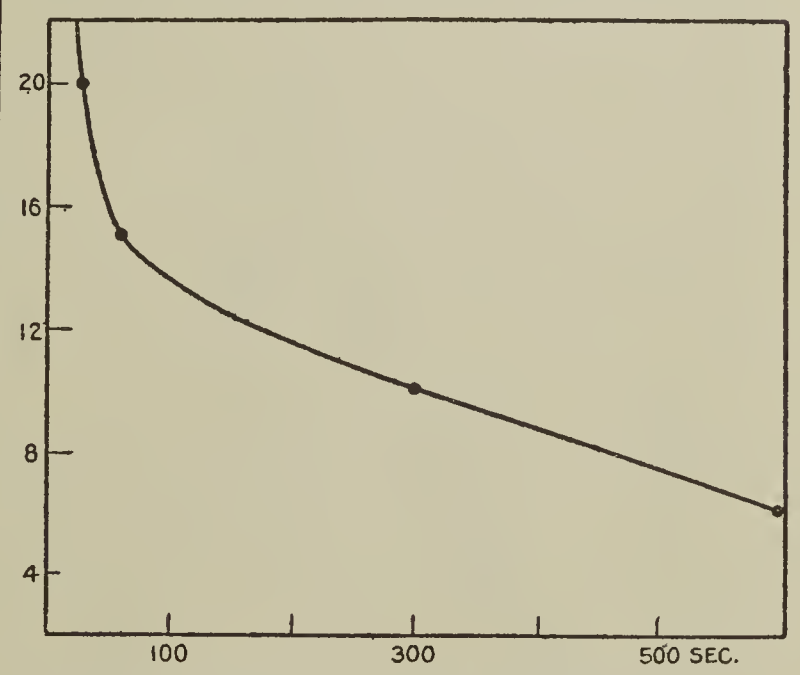


FIG. 166—Fatigue in brightness of ZnO at 1000° during incandescence (taken for 0.45μ)

Fatigue while unexposed is another property common to both types of luminescence here under consideration. That the glow from the newly formed particles of MgO in a flame of burning magnesium far exceeds that to be obtained if the oxide be collected and then reheated to the same temperature is well known. Similarly, many fluorescent crystals, when newly formed, exceed in brilliancy under excitation their subsequent intensity.

Sensitiveness to heat treatment may be referred to in this connection as a trait common to both types. Figure 152, in Chapter X, may be cited as showing that incandescent beryllium oxide may be greatly modified as to its brightness by modifying the temperature to which it had previously been brought.

[1] Nichols and Crehore. Phys. Rev. (1), II, p. 161, 1894.

Of the four attributes thus far considered, excess of brightness alone would lead to the certain classification of the radiation of these oxides as luminescence under the broad definition of Wiedemann. The others, *i. e.*, fatigue and recovery, sensitiveness to heat treatment, selectivity of spectral structure, are suggestive of a close relationship to ordinary fluorescence; taken collectively they are *very strongly* suggestive.

II. ESSENTIAL IDENTITY OF CATHODO- AND CANDO-LUMINESCENCE

(A) Cando-Luminescence and Photo-Luminescence of Oxides and Sulphides

A conclusive test would be the precise comparison of wave-lengths such as would be possible with radiations having line spectra. To detect and locate the submerged components of broad-banded spectra, particularly where luminescence is superimposed upon more or less powerful incandescence, is obviously more difficult than the analysis of the fluorescence spectra described in the earlier chapters of this treatise. Shortly after the discovery of excitation by the hydrogen flame (Chapter VIII), however, one of the writers undertook the following study of the glow thus produced.[1] The mesh of a disk of fine brass gauze was filled with air-slaked lime and was slowly rotated at a constant speed in grazing incidence with the flame. The size of the flame was kept as constant as possible by the use of a reducing-valve and a gas-regulator. Each spectrophotometric curve represents an average of many trials properly weighted.

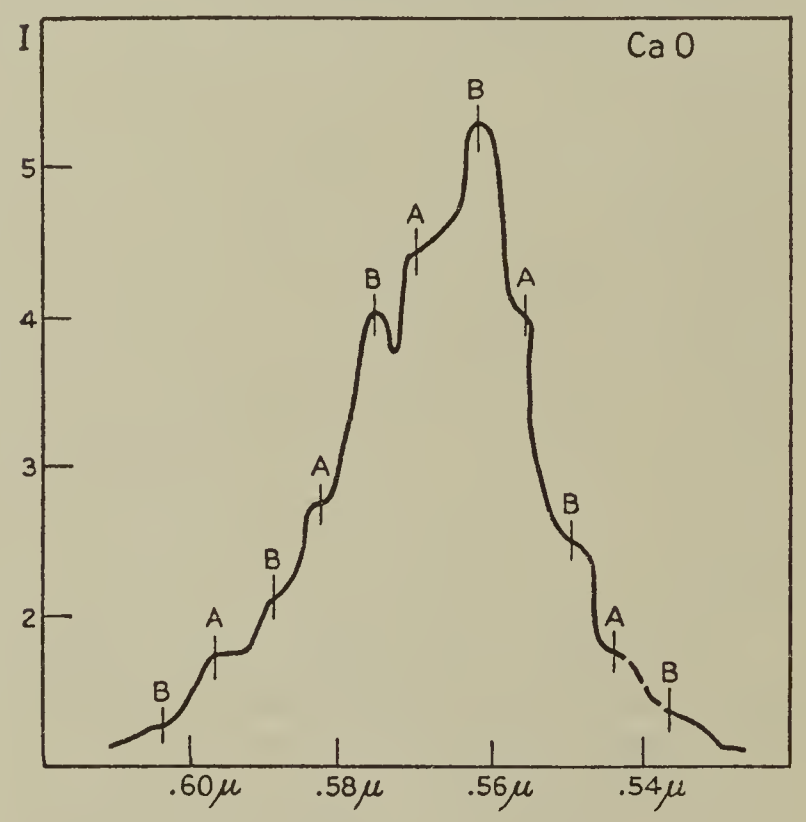


FIG. 167—Submerged components in the spectrum of CaO when excited by the H flame (cf. with fig. 169)

Figure 167 gives the distribution of brightness in the visible spectrum of the air-slaked lime. The luminescence was of an orange-yellow color characteristic of the band which extends between 0.61μ and 0.53μ as indicated in the curve. The maximum lies near 0.56μ. The subsidiary crests and shoulders, marked by short vertical lines, are not without a systematic arrangement. When the reciprocals of the wave-lengths of the crests are studied they are found to lie in two sets of a constant interval of 42 units, designated as the A and B sets. These wave-lengths and reciprocals are given in table

[1] Howes. Phys. Rev. (2), XVII, p. 469, 1921.

LXXVII, together with the wave-lengths previously obtained by excitation, with the iron spark, of natural calcite. (See Chapter II.)

The positions of the bands are *the same under the two different modes of excitation,* which indicates that when excitation by the hydrogen flame occurs, as has already repeatedly been shown to be the case for ordinary fluorescence, it is the activator which determines the spectral structure. Although the general form of the spectral envelope is quite different from that obtained by iron-spark excitation, the partially resolved crests are in no way shifted by change in mode of excitation. The form of the envelope in figure 167 corresponds more nearly to that for the calcite under the iron-spark excitation at 200° C. than at 20° C. (See fig. 18, in Chapter II.) This is naturally so, since the hydrogen flame warmed the specimen to a temperature of approximately 350° C. Temperature changes the relative intensities of the crests, but the A and B series are independent of both temperature and mode of excitation for their frequencies.

TABLE LXXVII—*Luminescence of lime*

Set A (interval 42)				Set B (interval 42)			
Band	Hydrogen flame	Iron spark	Frequency unit	Band	Hydrogen flame	Iron spark	Frequency unit
A_4	0.5975	0.5977	1,673	B_4	0.6045	0.6046	1,654
A_5	.5833	.5831	1,715	B_5	.5894	.5896	1,696
A_6	.5689	.5692	1,757	B_6	.5755	.5754	1,738
A_7	.5563	.5559	1,799	B_7	.5617	.5618	1,780
A_8	.5432	.5432	1,841	B_8	.5488	.5488	1,822
				B_9	.5365	.5365	1,864

The Lenard and Klatt sulphide known as No. 3 is a calcium compound containing bismuth as an activator. Since the spectral structure of this preparation had previously been studied under the excitation of the zinc spark, it was thought that an interesting comparison could be based on the resemblance between the zinc spark and hydrogen-flame excitation. The spectrum had been known to exhibit a strong band in the blue and a broader but much dimmer band in the orange. (See table II, in Chapter I.) Under hydrogen-flame excitation at a very moderate temperature the blue band was found in approximately the same location, but the orange band was of much greater proportionate intensity. To produce the orange band the mounting was rotated more slowly to allow a more favorable temperature. In some trials the specimen was mounted in the gauze without rotating, but in such cases every precaution was taken to maintain the temperature constant, but below red heat. A comparison of the location of the crests of the complex orange band under the two

different modes of excitation is given in table LXXVIII. One new band was found at 0.6360μ. The agreement is as good as could be expected, and no systematic deviation is evident. The components are undoubtedly in the same position and are spaced by a constant frequency-interval of 39 units. The spectrophotometric curve (fig. 168) is very dissimilar to that obtained by the zinc-spark excitation, as can be noted by comparison with the measurements of this sulphide described in Chapter II. In figure 168 the two wings of the curve are plotted to a greatly exaggerated scale to show components otherwise invisible.

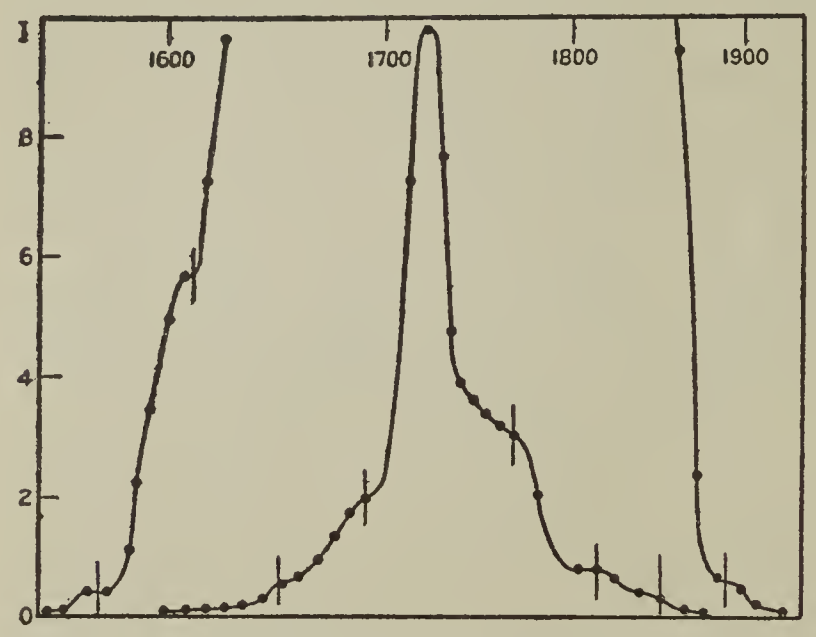


FIG. 168—Spectrum curve of a luminescent sulphide under H flame excitation

TABLE LXXVIII—*Luminescence of calcium bismuth sulphide No. 3*

Hydrogen flame	Zinc spark	Frequency-unit $1/\mu \times 10^3$	Frequency-interval
0.6365	.....	1,575	
			39
.6208	0.6200	1,614	
			39
.6048	.6049	1,653	
			39
.5912	.5910	1,692	
			39
.5785	.5781	1,731	
			39
.5650	.5650	1,770	
			39
.5530	.5528	1,809	
			39
.5415	.5411	1,848	
			39
.5300	.5300	1,887	

To make sure that the identity of band structure is not confined to this particular sulphide, another preparation of Lenard and Klatt containing strontium and bismuth was excited by the hydrogen flame. The spectral structure of this sulphide, which is known as Lenard and Klatt No. 13, has also been given in Chapter II. The undispersed light under flame excitation was of a delicate blue color and so dim that a considerable study of the method of mounting was necessary before sufficient radiation could be obtained to render spectrophotometric measurements possible. The light from the

4-c. p. comparison lamp was greatly reduced by interposing three or more sheets of white porcelain between it and the collimator slit. The field of view under these conditions was almost colorless and the time required for eye accommodation about 30 minutes.

To bring out the comparison of results of the two modes of excitation, a portion of the curve for fluorescence due to the zinc spark is reproduced in figure 169 (curve *Z*) and the corresponding curve for excitation by the hydrogen flame (curve *H*). The component of shortest wavelength, 0.4546μ, table LXXIX, is beyond the range of the diagram. The curve *H* represents one side of a broad band of a relatively great intensity extending into the violet or ultra-violet, the crest of which can not be determined by means of the spectrophotometer. As is indicated in table LXXIX and in fig-

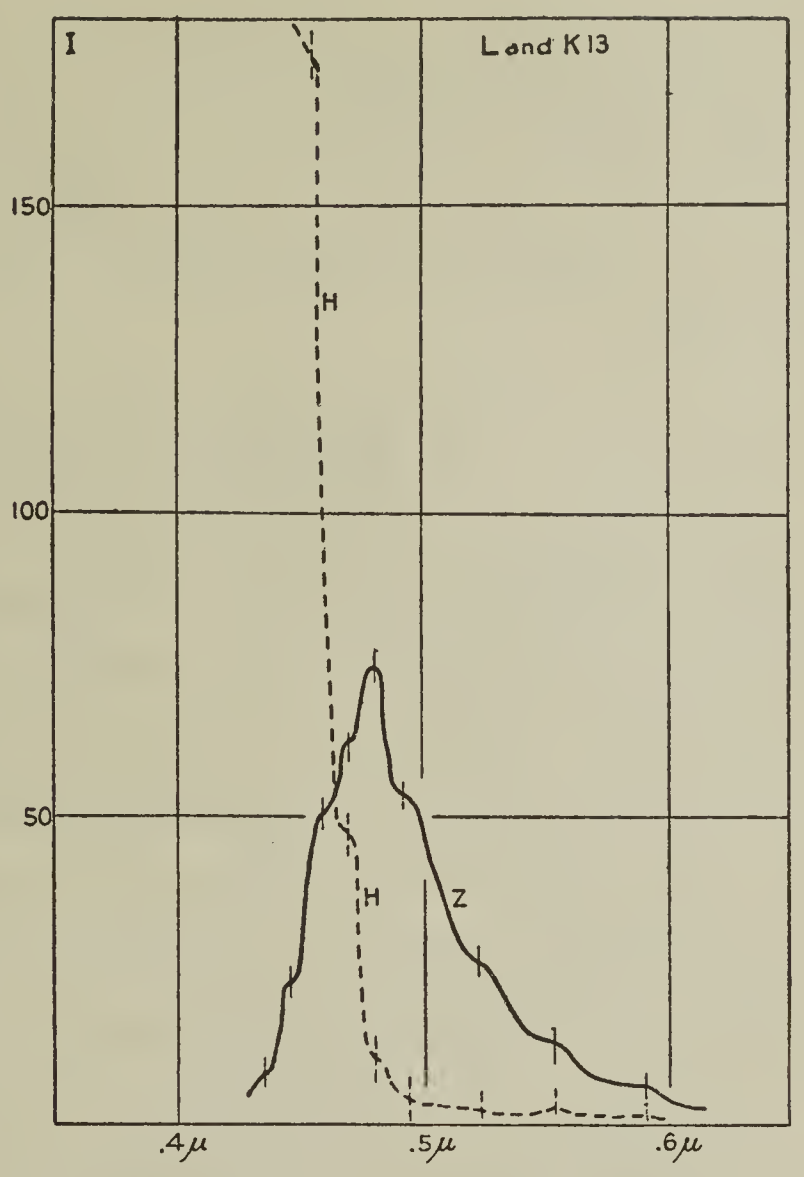


FIG. 169—Submerged components in the spectrum of a phosphorescent sulphide when excited by a zinc spark (*Z*) or by the hydrogen flame

TABLE LXXIX—*Luminescence of strontium bismuth sulphide No. 13*

Hydrogen flame	Zinc spark	Frequency unit $1/\mu \times 10^3$	Frequency interval
0.5565	0.5562	1,793	
			58
.5414		1,851	
			58
.5235	.5238	1,909	
			58
.5080	.....	1,967	
			58 } =4×14.5
.4938	.4938	2,025	
			58
.4800	.4801	2,083	
			58
.4668	.4670	2,141	
			58
.4546	.4547	2,199	

ure 169, it is made up of the same set of components as those occurring in the photo-luminescence band *Z*.

The interval for this sulphide as given in the table is quite consistent with the presence of bismuth as an activator, since within the errors of observation it is an exact multiple of the Tanaka ratio 14.6 for series I of that element. (See Chapter III, table VIII, part 42.)

(B) The Spectra of Incandescent Fluorites

[Experiments of L. J. Boardman.]

The foregoing experiments establish the essential identity of the spectra of substances excited to fluorescence by the hydrogen flame and by the usual agents, such as ultra-violet light and cathode rays. They do not, however, fully cover the case of the luminescence of incandescent solids, since a substance excited by contact with the active layer of the flame frequently is below the red heat in temperature. Dr. Boardman, however, who for some time has been engaged in the attempt to extend the analysis of banded spectra with submerged components to the study of the spectra of incandescent solids, furnishes the following facts bearing directly upon the question of the spectrum of the luminescence of incandescent calcium oxide.

Dr. Boardman, in the course of his investigation, photographed the spectrum of an incandescent bead of fused fluorite mounted upon a platinum wire within a hydrogen flame. Upon measurement of the negatives by the method described in the chapter on photographic studies (Chapter V), *eighty-three* submerged components were revealed. These extend from the deep-red 0.7215μ into the near ultra-violet 0.3839μ. Most of them arrange themselves in six or more sets having the interval 42, from which we infer that the dominant activator is manganese. One of these sets is strictly coincident with set A in table LXXVII, page 333, the band 1,757 being the only one found in the cathode and H-flame spectra which did not appear in the list of bands found in the photographs of the incandescent lime in the bead. This set is represented in the latter spectrum by at least three members of greater wave-length, not picked up visually, and of at least ten toward the violet beyond the limits of the measurably visible group.

Set B of table LXXVII appears at first glance not to conform to this analysis, there being but one band of the six listed in the table with which the spectrum of the incandescent oxide coincides. There are, however, four bands of this set in the red beyond the edge of the measurably visible group and at least four in the violet.

The evidence seems quite sufficient, considered in connection with numerous other analyses of these broad-banded spectra, to warrant

the conclusion that whatever may ultimately be found to be the mode of excitation in the luminescence of incandescent solids, we have a spectral structure essentially identical with that of fluorescence of the ordinary well-known type.

OBSERVATIONS ON TRANSFORMATION SPECTRA

To many minds the observation of bands directly visible may seem to offer more convincing evidence upon the point here at issue than can be derived from submerged components of a broad-banded or apparently continuous spectrum. Such bands, so far as luminescence at high temperatures is concerned, are to be looked for chiefly where the rare earths are activators. A significant instance is that of the transformation spectra described in the foregoing chapter, where bands that could be identified as characteristic of the fluorescence of solids containing samarium, europium, terbium, etc., were observed in the spectra of incandescent beads containing traces of those elements. When we add, as was found to be the fact, that such bands appeared only when the substance was passing through the temperature at which by previous measurements outbursts of luminescence occur, the observation of the bands gains greatly added force in the argument for the oneness of fluorescence, from the incandescent ranges down to the temperatures of liquid air or liquid hydrogen.

In the course of a description of some low-temperature investigations made in the laboratory of Kammerling-Onnes 20 years ago, Henri Becquerel[1] introduces the following statement:

> "Si l'on examine avec un spectroscope la flamme d'un bruleur a gaz dans laquelle on introduit au bout d'un fil de platine un petit fragment de fluorine on observe un spectre de bandes analogue a ceux qu'emettent par phosphorescence les fluorines, soit dans le phosphoroscope sous l'influence de la lumiere, soit lorsqu'on les echauffe, soit lorsqu'on les excite par des rayons cathodiques.
>
> "En juxtaposent dans le spectroscope l'un de ces derniers spectres avec le spectre de la flamme en question, on observe la coincidence de plusieurs groupes de bandes et l'absence de certaines autres dans le spectre de la flamme."

Here is a statement of an observation which, perhaps because of its unlooked-for position in the literature, has only at the time of writing come to our knowledge. With it our recent discovery of transformation spectra is in complete accord, affording a striking confirmation. In corroboration of both experiments, we now have also photographs by Boardman of the spectra of fluorites, in which are found these characteristic bands of the rare earths hitherto known only in the cathodo-spectra.

[1] Henri Becquerel, C. R. CXLVI, 1908, p. 154.

To compare further the spectrum of fluorite brought to incandescence with that of the same material under cathodo-bombardment, one of the fluorspars studied by Miss Wick was selected. From her work, already described in Chapter V, this specimen was known to have a luminescence spectrum containing numerous line-like bands due to traces of the rare earths.

Photographs of the spectrum at the temperature favorable to the development of cando-luminescence (1200° C.) were made by spreading a layer of the crushed crystals upon an alundum disk and bringing the material to the required state of incandescence by means of a properly adjusted oxy-hydrogen flame. The continuous spectrum of the background masked the bands so completely, however, that this procedure was abandoned.

The method subsequently employed was that of gradually introducing the powdered fluorite directly into the flame. When a narrow cylindrical flame of hydrogen, slightly reinforced with oxygen, was used, a sufficient number of the glowing particles passed through the required range of temperatures to bring out the bands in the spectrum. Some of the luminescence bands thus obtained were fully as bright as the strongest of the calcium-vapor lines. After heating according to the method described by Miss Wick, the spectrum of the cathodo-luminescence of the same fluorspar was then repeatedly photographed. Both sets of photographs were mapped by means of the apparatus developed by Mr. Fisher (Chapter V).

TABLE LXXX—*Narrow bands in the flame and cathodo luminescence of fluorspar*

1	2	3	4	1	2	3	4
Both spectra	Flame only	Cathodo only	Bands from Urbain's tables	Both spectra	Flame only	Cathodo only	Bands from Urbain's tables
.....	7,550	.....	Dy abs	.....	.....	5,643	Sa, Eu
.....	7,290	.....	.....	5,555	.....	.....	Sa, Er
.....	7,155	.....	.....	5,513	.....	.....	Tb, Ca
.....	6,895	.....	.....	.....	.....	5,484	Sa
6,690	.....	.....	Pr	.....	5,425	.....	Tb, Ca
.....	.....	6,540	.....	.....	.....	5,397	.....
.....	6,480	.....	Sa, Er abs	.....	.....	5,358	Pr
.....	.....	6,445	Sa	5,326	.....	.....	Tb, Er
6,405	.....	.....	.....	.....	5,301	.....	Sa
.....	.....	6,295	Ne abs	5,250	.....	.....	Pr, Eu abs
.....	6,265	.....	Sa, Pr	5,224	.....	.....	Er abs
6,200	.....	.....	Pr	5,187	.....	.....	Er, Eu
6,115	.....	.....	.....	.....	5,174	.....	.....
.....	.....	6,010	Tb, Sa	.....	.....	5,165	Pr
.....	.....	5,930	Eu	5,111	.....	.....	Ne
.....	5,885	.....	Tb, Pr, Eu	.....	5,090	.....	.....
5,802	.....	.....	Ne abs	.....	.....	5,076	.....
5,714	.....	.....	Ne abs	5,028	.....	.....	Tb

TABLE LXXX—*Narrow bands in the flame and cathodo luminescence of fluorspar*—Con.

1	2	3	4	1	2	3	4
Both spectra	Flame only	Cathodo only	Bands from Urbain's tables	Both spectra	Flame only	Cathodo only	Bands from Urbain's tables
4,990	.....	.....	Sa abs	.....	4,150	.....	.....
4,954	.....	.....	Dy	4,116	.....	.....	.....
.....	4,935	.....	.....	.....	4,096	.....	.....
4,924	.....	.....	.....	.....	.....	4,090	.....
4,885	.....	.....	Dy	.....	.....	4,081	Sa abs
4,848	.....	.....	Er abs	.....	4,077	.....	.....
4,815	.....	.....	Pr abs	.....	.....	4,071	Sa abs
4,783	.....	.....	Tb, Sa abs	.....	4,062	.....	.....
4,760	.....	.....	Tb, Sa abs	4,046	.....	.....	.....
4,742	.....	.....	Ne abs	.....	.....	4,039	.....
4,728	.....	.....	Tb	.....	4,032	.....	.....
4,716	.....	.....	.....	4,016	.....	.....	Sa abs
.....	4,705	.....	Ne abs	4,005	.....	.....	Sa abs
4,675	.....	.....	Dy	.....	.....	3,993	.....
4,661	.....	.....	Ne, Eu abs	3,981	.....	.....	Ne
4,633	.....	.....	Dy, Sa abs	3,971	.....	.....	Dy, Ca
.....	4,614	.....	Ne	3,954	.....	.....	Eu abs
4,568	.....	.....	Tb	.....	3,938	.....	.....
.....	4,549	.....	.....	3,924	.....	.....	Ne
.....	4,540	.....	Dy	.....	3,912	.....	Tb
.....	.....	4,531	Sa abs	3,905	.....	.....	Sa abs
4,515	.....	.....	Ne	3,898	.....	.....	.....
4,497	.....	.....	Er abs	.....	3,881	.....	Tb, Ca
4,482	.....	.....	.....	3,875	.....	.....	.....
4,457	.....	.....	Tb	3,866	.....	.....	Tb
.....	4,429	.....	Sa abs	.....	.....	3,846	.....
.....	.....	4,424	Er abs	.....	3,838	.....	Eu
4,409	.....	.....	Tb	3,830	.....	.....	.....
.....	.....	4,396	Tb	.....	.....	3,819	.....
.....	4,385	.....	.....	.....	3,815	.....	.....
.....	4,367	.....	Tb	.....	3,805	.....	Tb
4,353	.....	.....	Tb	3,798	.....	.....	Tb
4,335	.....	.....	.....	3,786	.....	.....	Tb
4,319	.....	.....	.....	3,777	.....	.....	Tb
.....	4,304	.....	.....	3,769	.....	.....	Tb
.....	.....	4,296	Ne	3,760	.....	.....	Eu abs
.....	4,287	.....	Ne, abs	.....	.....	3,752	Sa abs
.....	4,271	.....	Ne	3,744	.....	.....	Eu
.....	.....	4,265	.....	.....	.....	3,739	Sa abs
.....	.....	4,249	.....	.....	3,736	.....	Tb
4,227	.....	.....	Ne	.....	.....	3,730	.....
.....	4,210	.....	Tb	3,720	.....	.....	Tb
4,192	.....	.....	Ne, Tb	3,712	.....	.....	.....
.....	4,183	.....	Tb	.....	.....	3,703	.....
.....	.....	4,174	.....	3,694	.....	.....	Tb
.....	4,168	.....	Sa abs	.....	3,670	.....	.....
4,159	.....	.....	Tb				

In table LXXX, column 1 gives the location of bands occurring in both spectra, column 2 those found in the flame spectrum only, and column 3 those found only in the spectrum of the crystals excited to cathodo-luminescence at room temperature. Column 4 indicates the activator to which the various bands, in so far as they could be

identified, were ascribed. The data of Urbain for the cathodo-luminescence of various rare earths, etc., in CaO as a solvent were used for comparison.

Of the 129 bands which reappeared consistently in the photographic records and were therefore listed in table LXXX, 86 correspond to bands in Urbain's table; 62 of the bands are common to both spectra; 38 appeared in the photographs of the flame spectrum only, and 29 in the spectrum of the fluorspar when excited by cathode rays.

When we consider the large number of possible activators present in this fluorspar, the great difference of temperature, and that two entirely different modes of excitation were employed, the approach to complete coincidence is remarkable. The essential identity of the two spectra would seem to be established beyond any reasonable doubt.

The identification of bands by comparison with Urbain's tables is not free from difficulty, especially as his spectra were relatively broad-banded and diffuse. Boardman finds:

Bands presumably due to—	
Terbium	29
Samarium	22
Neodymium	16
Europium	10
Erbium	8
Præsodymium	8
Dysprosium	7

(C) Activators at High Temperatures

Whether under conditions of incandescence, luminescence is dominated by activators (as is the case with luminescence at ordinary temperatures), perhaps may be regarded as a no less important test of the identity of the two effects than is spectral structure. For as we have shown, at ordinary temperatures spectral structure, brightness, and to a high degree color also, may be controlled by the merest trace of copper, manganese, uranium, or a rare earth. In the course of our studies of incandescent solids we observed the luminescence of two substances well suited to exhibit the effects of activators. These were:

(1) A sample of aluminum oxide with an admixture of chromium, as in the making of synthetic rubies. (A finely phosphorescent preparation for which we are indebted to Mr. W. S. Andrews.)

(2) A crystal of fluorite showing, after proper heating, the narrow line-like bands in its cathodo-luminescence due to the presence of traces of rare earths. (This was one of the specimens then under spectrographic observation by Miss Frances G. Wick; see Chapter V.)

When incandescent these specimens showed the rather complicated outbursts of luminescence depicted in figures 170 (ruby) and 174

(fluorite), respectively. These were observed through three color-screens, successively, with the following results:

The ruby—Inspection of figure 170 leads at once to the recognition of two distinct bands in the luminescent radiation. One of these occupies the part of the spectrum visible through the "blue" screen (equivalent wave-length 0.45μ). This band attains very great relative intensity (at least 1,540 times that of the black-body radiation) for some temperature well below 1000° C. and probably near the

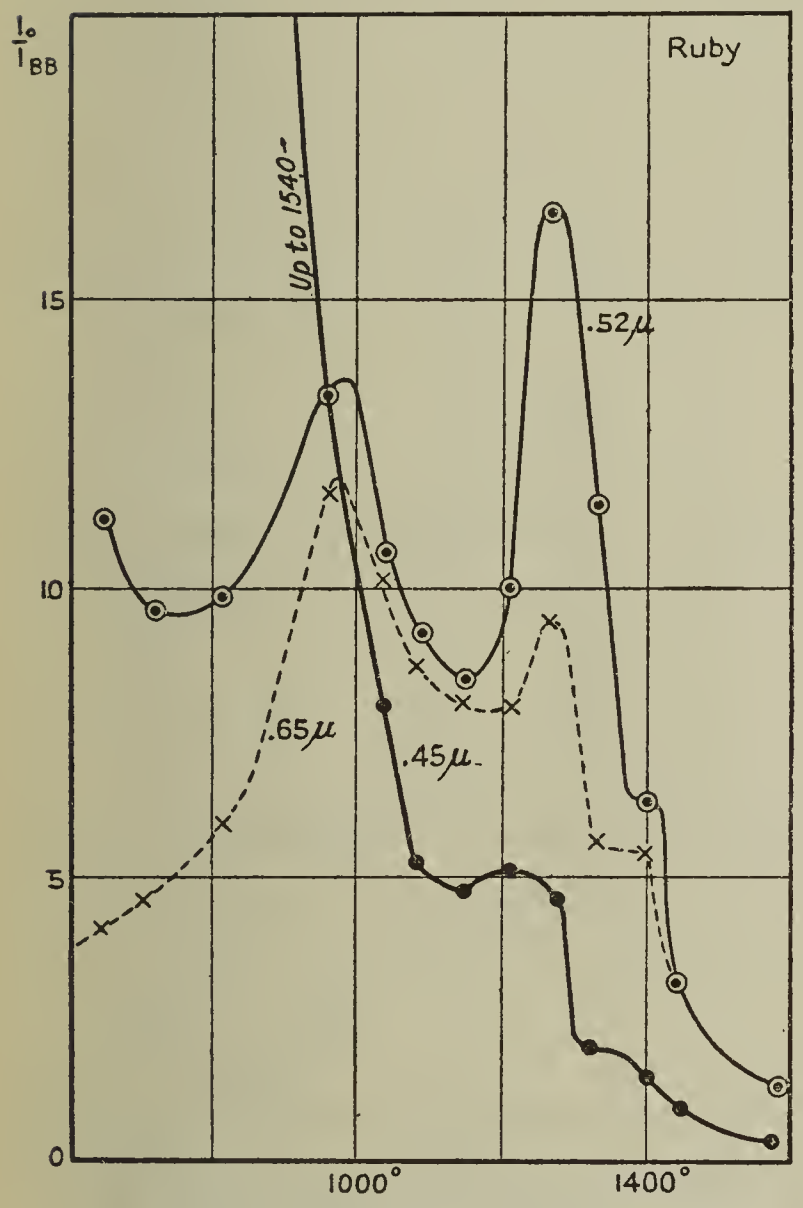


Fig. 170—Luminescence of the incandescent ruby

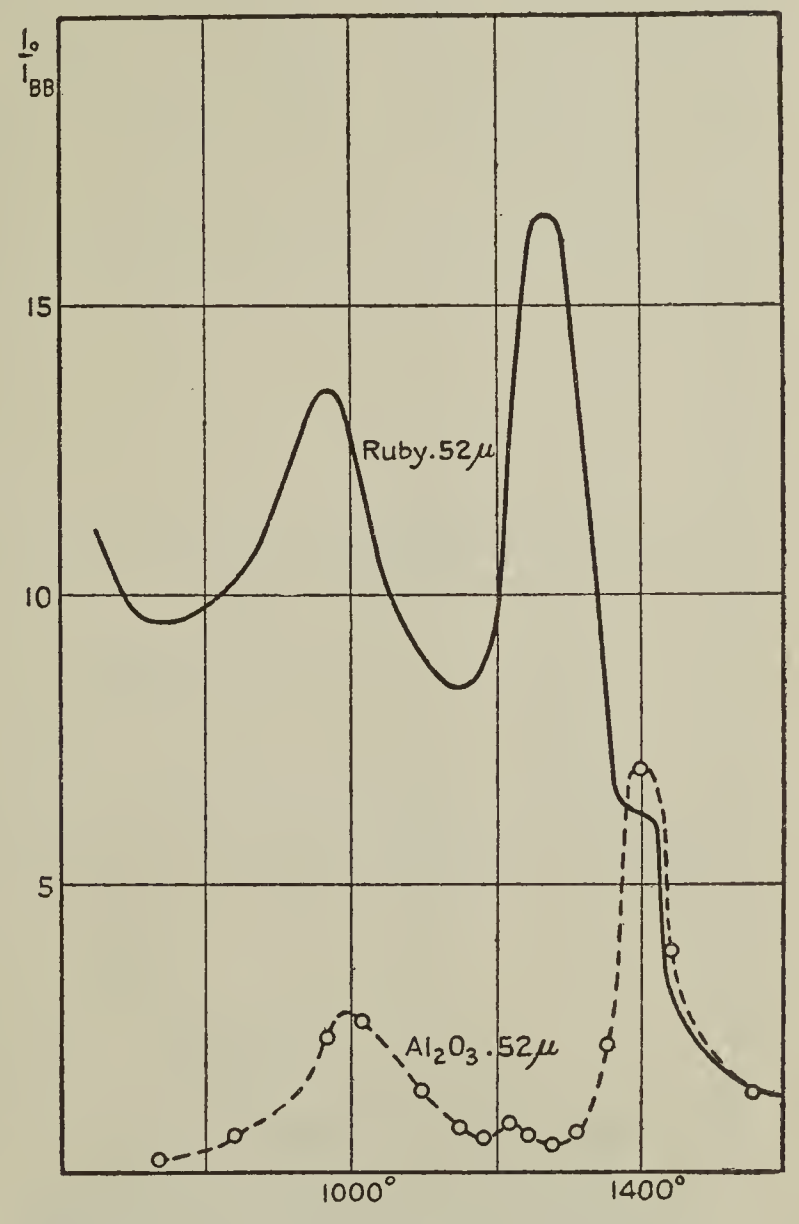


Fig. 171—Luminescence of Al_2O_3 and the ruby as seen through the green screen

threshold of incandescence. In other words, it affords a marked example of the "blue glow." On the other hand, the regions visible through the "red" (0.65μ) and "green" (0.52μ) screens are but little affected by the blue glow; the green very slightly, the red not perceptibly. Both of these regions, however, show marked luminescence just below 1000° and at about 1275°.

To determine as far as may be possible by this method in how far these departures from black-body radiation are attributes of Al_2O_3, which forms the solvent, and what effect is to be assigned to the trace of chromium, the activator, these curves should be compared with

those for Al_2O_3 in Chapter X (fig. 136). For convenience of comparison, the curves for each of the three colors (0.45μ, 0.52μ, and 0.65μ) are plotted to the same scale separately in figures 171, 172, and 173 for Al_2O_3 and the ruby. In figure 171 (0.52μ) we note that:

(1) For all temperatures below 1400° the brightness of luminescence is *greatly enhanced* by the presence of the activator, while above 1400° the curves become practically identical.

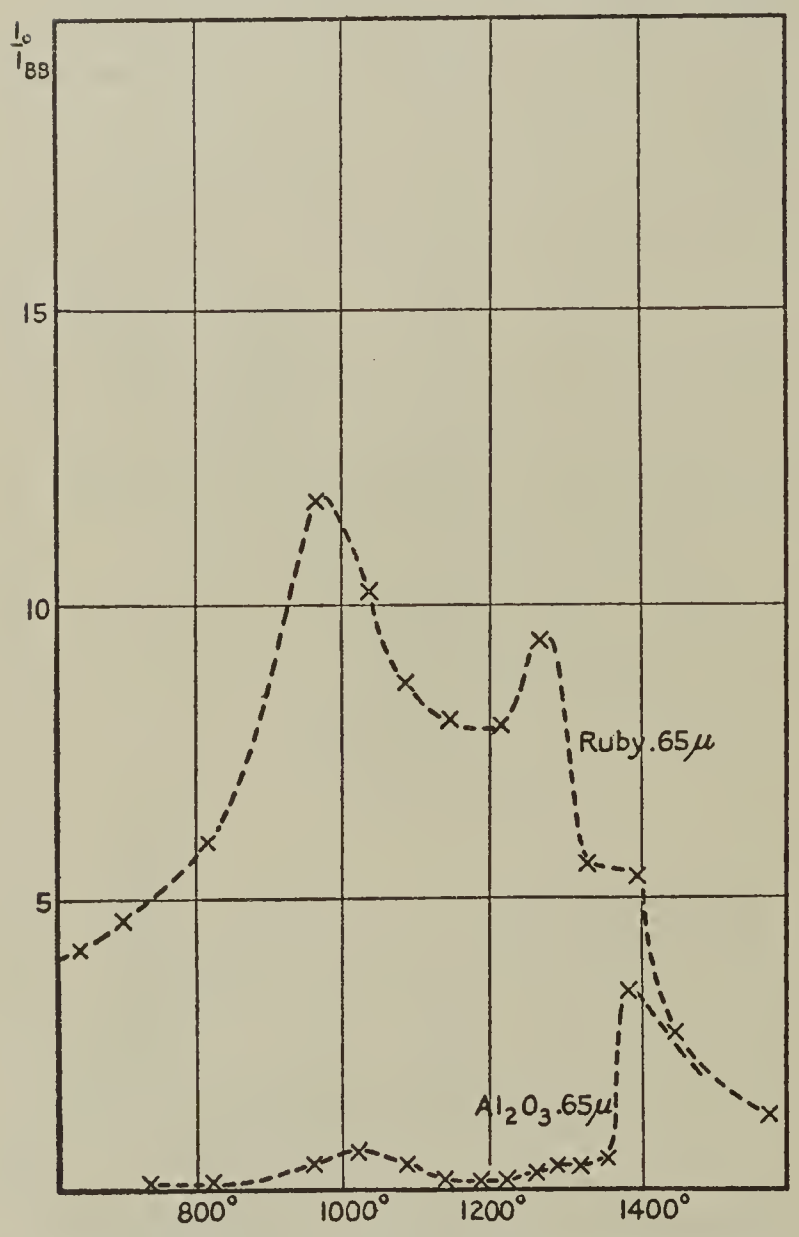


FIG. 172—Great enhancement in the red of the luminescence of the ruby due to activation by chromium

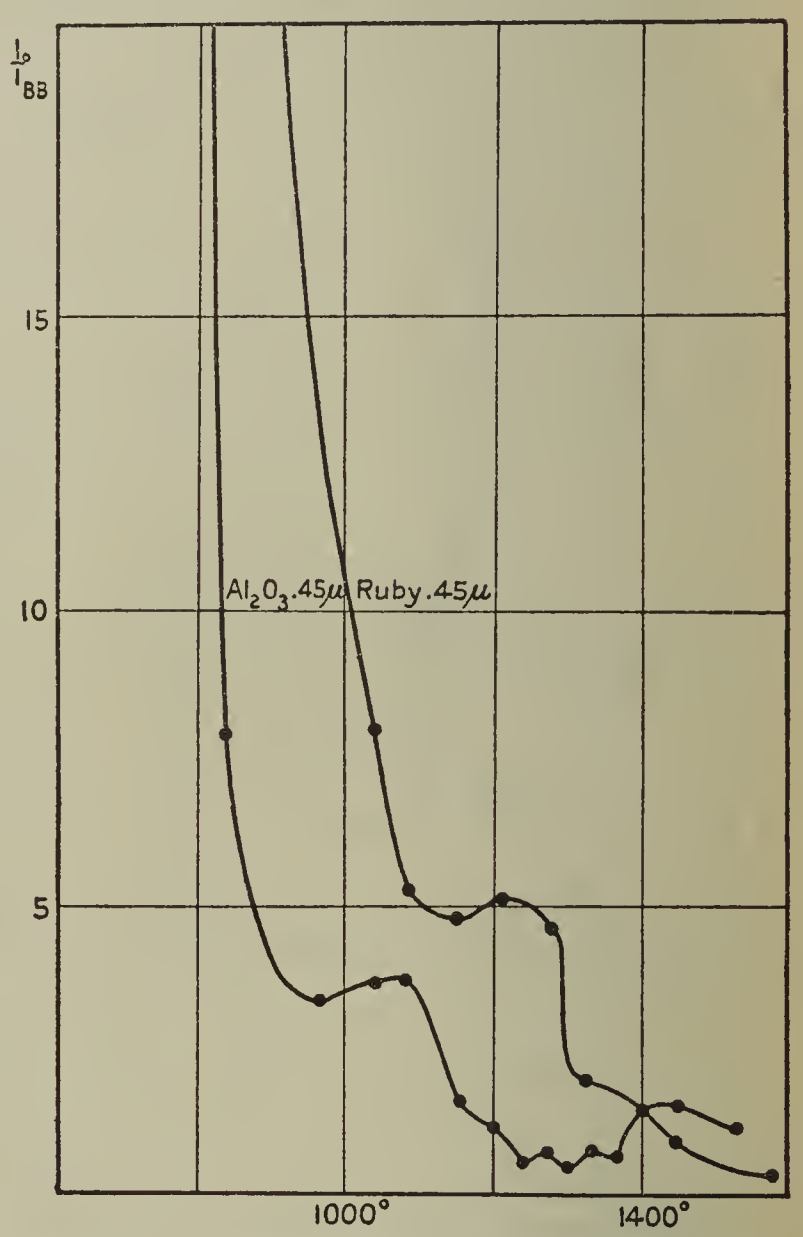


FIG. 173—The blue-violet luminescence of Al_2O_3 and the ruby

(2) Of the two outbursts which occur at transformation temperatures of Al_2O_3, *i. e.*, just below 1000° and at 1400°, the former is prominent in the curve for the ruby, while the latter is largely suppressed, being represented only by a shoulder upon the curve.

(3) That the strongest manifestation of luminescence in this part of the spectrum occurs at about 1275° C., at which temperature the radiation from Al_2O_3 is at its lowest, or about 40 per cent of the corresponding black-body radiation. It is understood that in all these diagrams the ordinates are the ratio of I_0, the radiation from the oxide or other luminescent substance, to I_{bb}, the corresponding black-body radiation for the given temperature and wave-length. Black-body

radiation would therefore be represented by a horizontal line of ordinate unity.

We have here actions which are highly characteristic of the effects of activators in ordinary fluorescence, *i. e., marked enhancement and a tendency to suppress luminescence due to other sources.*

In figure 172 we note even greater enhancement throughout the entire range of temperature up to 1400°. In this part of the spectrum the radiation from pure Al_2O_3 never approaches black-body intensity until the outburst at 1400° is reached. Above that temperature both curves coalesce, as in figure 173, and approach black-body intensity in the manner characteristic of the radiation of all these oxides after the range of temperatures at which luminescence occurs has been passed.

In the curve for Al_2O_3 in both figures 171 and 172 there may be noticed a slight suggestion of an accession of brightness above 1200° which perhaps corresponds to the crest of luminescence in the ruby. It may be due to an exceedingly small amount of chromium present in the oxide, an amount far below the optimum. In figure 173 is a record of attempts to estimate brightness at various temperatures in the part of the visible spectrum where the greatest instability seems to prevail and where almost inappreciable fluctuations of the exciting flame suffice to produce wholly disproportionate variations in luminescence. The enhancement of the ruby in the lower ranges is, however, evident; also two crests of Al_2O_3 which are supported in the ruby by one of intermediate temperature.[1]

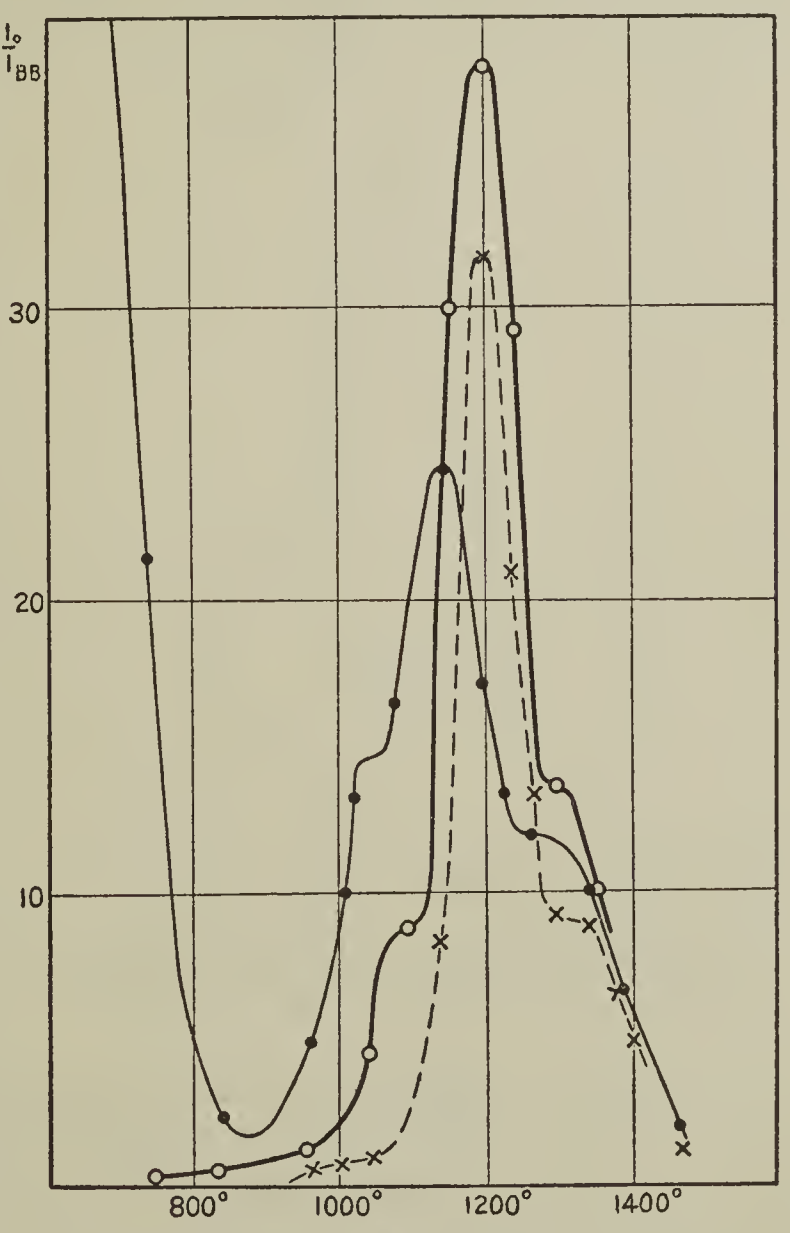


FIG. 174—Luminescence crests of fluorite containing samarium

[1] Another striking instance of the effect of an activator was observed in the luminescence of columbium oxide. This sample was known to be impure. It did not agree as to melting-point with the columbium oxide described in Chapter X. The blue glow of this material was so intense as to be measurable at 560° C., at which tempera-

The fluorite—The activator present in the specimen of fluorite whose luminescence is depicted in figure 174 was not definitely known at the time of our measurements, but it would have been quite justifiable to name samarium as that activator after a comparison with the curves for samarium oxide in Chapter X (figs. 143 and 144). We now know from the work of Miss Wick that the element was present and dominant.

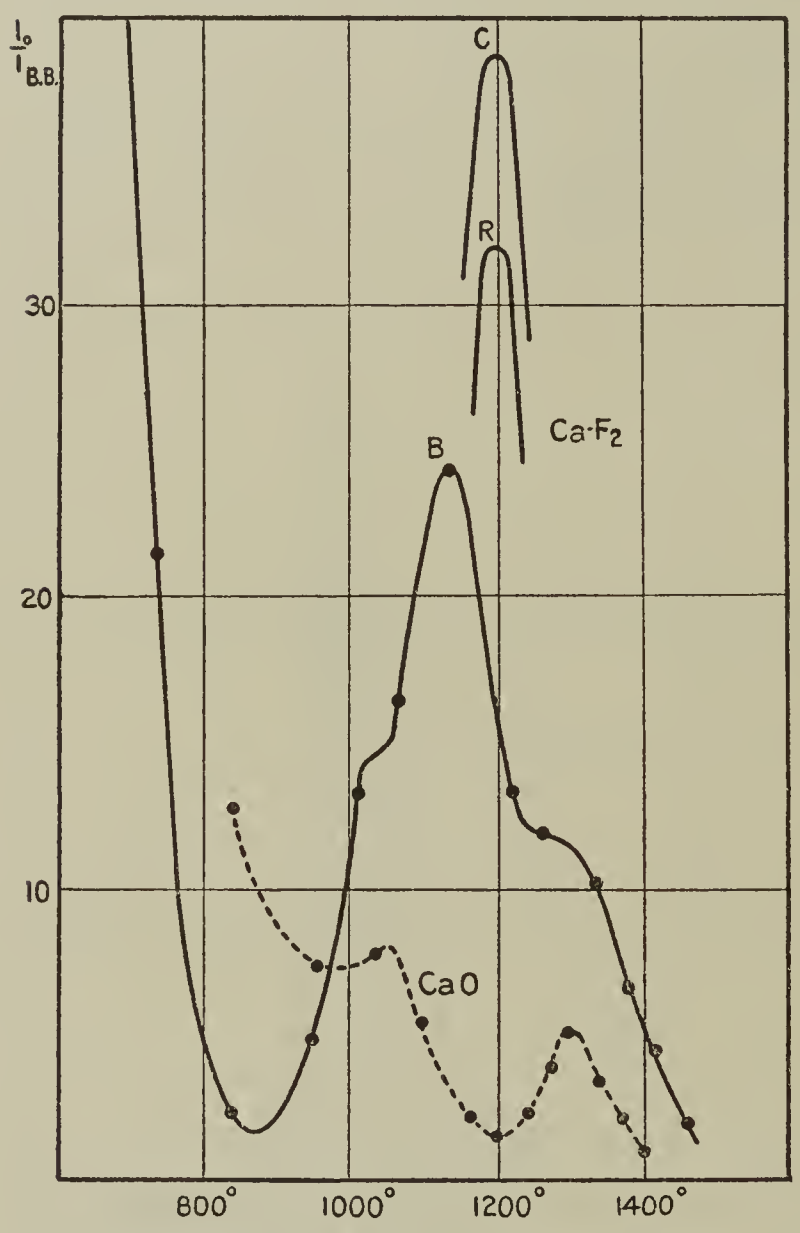


FIG. 175—Luminescence of fluorite (0.45 ?) with curve for CaO and the red and green crests of fluorite (*R* and *G*)

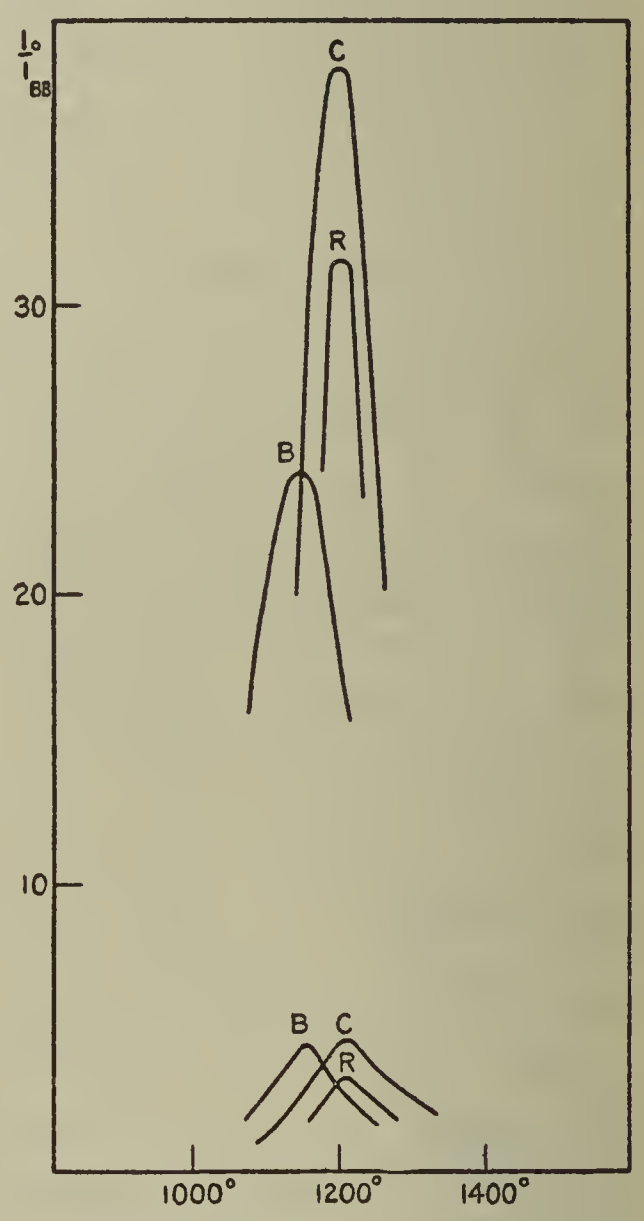


FIG. 176—Fluorite and samarium oxide (showing enhancement)

The crests in figure 174 do not correspond in temperature with the crests of CaO, which must be taken as the solvent rather than CaF_2 in the radiating surface layers of a crystal of fluorspar when heated to the temperatures in question in an oxy-hydrogen flame. The shoulders of the curves do, however, represent the crests of the CaO curve, as may be seen in figure 175, where that curve is dotted in for comparison. The *crests,* however, are distinctly assignable to the

ture the value of I_o/I_{bb} for 0.45μ was 85,200. (See Nichols and Howes, Phys. Rev. (2), XIX, p. 311.) At 655° the ratio was 2,150 or nearly 40 per cent greater than for the ruby depicted in figures 170 to 173. The nature of the activator is unfortunately unknown.

element samarium, but greatly enhanced, as appears in figure 176. where the three crests for fluorite are shown at the top of the diagram and the corresponding crests for samarium oxide drawn to scale at the bottom. The samarium crests are from a sample of that oxide *heated in bulk* instead of being greatly diluted in a solid solvent.

CONCLUDING STATEMENT

It has been the purpose of this treatise, and particularly of this final chapter, to bring together the accumulating evidence connecting the luminescence of incandescent bodies with the fluorescence of solids at ordinary temperatures. We think, in view of the facts here presented, that the luminescence superimposed upon the incandescence of the various solids is simply a *fluorescence* in all essentials identical with that commonly excited by light, cathode rays, and other familiar agencies.

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